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THE SILVER VOLTAMETER—PART III

SECOND SERIES OF QUANTITATIVE EXPERIMENTS AND THE PREPARATION AND TESTING OF SILVER NITRATE

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I. QUANTITATIVE EXPERIMENTS, SECOND SERIES

A. INTRODUCTION

The second series of quantitative experiments began on December 17, 1909, after several months spent in the work described in the second paper.[1] The first series had been chiefly concerned with the investigation of the filter paper voltameter, and, together with the qualitative investigations, had demonstrated the action of filter paper on the silver nitrate to be so considerable as to make this form of voltameter unreliable for work of high precision. In the present series of experiments attention was directed chiefly to the porous pot and nonseptum forms of voltameters. The apparatus and methods used were similar to those previously employed which have been described in the first paper.[2] Some of the problems studied were the so-called "volume effect," the trouble from anode slime in the Poggendorff form and the cause of used solutions yielding somewhat lower values for the electrochemical equivalent than new solutions when filter paper is excluded.

[1] This Bulletin, 9, p. 209, Reprint No. 195.

[2] This Bulletin, 9, p. 157, Reprint No. 194.

B. GENERAL TABLE OF RESULTS

Between December 17, 1909, and April 5, 1910, 156 deposits of silver were made, which are recorded in Table 1. In the column giving the electrochemical equivalent of silver the results are expressed in milligrams per coulomb, which is based on the Weston Normal Cell having a voltage of 1.01890 at 25° C, because this is the value which was in use in the United States prior to January 1, 1911. In the subsequent tables the results have been classified according to the form of voltameter in which they were made. In these tables the original figures for the electrochemical equivalent are given, and in addition the voltage of the Weston Normal Cell computed from the weight of deposit, the time, and the electrochemical equivalent of 1.11800 mg. per coulomb as specified by the London Conference of 1908. In doing this, however, a correction of three parts in 100 000 to our electrical standards has been found necessary and has been applied.[3]

The electrolytes are designated as before. "Baker" means $AgNO_3$ from the J. T. Baker Chemical Co., of Phillipsburg, N. J., while "Frankfurt" indicates that the salt was procured from the Gold- und Silber- Scheide- Anstalt of Frankfurt, Germany. In some cases it has been recrystallized by ourselves, in which case this fact is noted.

[3] Report of the International Technical Committee, p. 26.

TABLE 1

General Table of Quantitative Results for 1910

Date	No.	Bowl	Form	Electrolyte	Time	Current	Deposit	Electro-chemical equivalent	Remarks
1909					sec.	amp.	mg		
Dec. 17	122	95	Richards	Frankfurt 15%			4097.16	1.11705	Large porous cup
	123	93	Poggendorff	Frankfurt 10%			4102.45	849	Without silk; anode slime on cathode
	124	92	Richards	do			4097.38	711	Large porous cup
	125	26	do	do			97.02	701	Do.
	126	127	Poggendorff	Frankfurt 15%	7200.00	0.509424	98.19	733	Without silk
	127	128	do	do			98.41	738	Do.
	128	27	Richards	do			96.93	698	Small porous cup
	129	28	do	do			97.27	707	Coarse porous cup
	130	125	do	do			96.98	700	Small porous cup
	131	126	do	do			97.10	703	Do.
1910									
Jan. 7	132	95	Rayleigh	Baker 10%			4098.84		Less filter paper than usual
	133	93	Siphon	do			99.55		Volume of liquid, 500 cc
	134	92	do	do			99.57		Do.
	135	26	Richards	do			98.24		
	136	127	Poggendorff	do			99.31		Without silk
	137	128	do	do	2 hours	½ amp.	99.26		Do.
	138	27	Richards	do			98.04		
	139	28	do	do			98.74		Coarse porous cup
	140	125	do	do			98.10		
	141	126	do	do			97.97		

13	142	95	Siphon	Frankfurt 10%			4097.27		500 cc of electrolyte
	143	93	do	do			97.32		Do.
	144	92	Richards	do	2 hours	½ amp.	96.59		Large porous cup
	145	27	do	do			96.34		
	146	28	do	do			96.34		
21	147	95	Siphon	Used Frankfurt filtered			4149.11		
	148	93	do	do			48.58		Porous cup on cathode end of siphon
	149	92	Richards	do			48.86		Small porous cup
	150	26	do	New Frankfurt filtered			48.76		Large porous cup
	151	127	Poggendorff	Used Frankfurt filtered	2 hours	½ amp.	48.61		
	152	128	do	New Frankfurt filtered			48.58		Without silk
	153	27	Richards	Used Frankfurt filtered			48.47		Do.
	154	28	do	New Frankfurt filtered			48.34		Coarse porous cup
	155	125	do	Used Baker filtered			46.52		Abnormal
	156	126	Rayleigh	New Frankfurt filtered			50.37		One sheet filter paper
26	157	27	Richards	Frankfurt 10% filtered			4096.78	1.11687	Pasteur filter No. 1 used
	158	28	do	Frankfurt 10%	7200.90	0.509372	97.41	704	Not filtered
	159	125	do	do			97.56	709	Do.
	160	126	do	Frankfurt 10% filtered			96.91	691	Pasteur filter No. 1 used
28	161	27	do	Frankfurt 10%			4096.97	1.11702	Not filtered
	162	28	do	Frankfurt 10% filtered			96.89	700	Pukal bulb used as filter
	163	125	do	Frankfurt 10%	7199.86	0.509422	96.94	701	Not filtered
	164	126	do	Frankfurt 10% filtered			96.93	701	Pukal bulb used as filter
31	.....	27	Asbestos	Frankfurt 10%			.....	.....	Asbestos mat disintegrated
	165	28	Richards	do	2 hours	½ amp.	4163.51	.....	Platinum cathode
	.....	125	Asbestos	do			.....	.....	Asbestos mat disintegrated
	166	126	Richards	do			63.55	.....	Gold cathode
Feb. 3	167	27	do	do			4130.93	.....	
	168	28	do	Frankfurt 15%	2 hours	½ amp.	30.89	.....	
	169	125	do	do			30.84	.....	
	170	126	do	Frankfurt 10%			30.95	.....	

TABLE 1—Continued

General Table of Quantitative Results for 1910—Continued

Date	No.	Bowl	Form	Electrolyte	Time	Current	Deposit	Electro-chemical equivalent	Remarks
					sec.	amp.	mg.		
Feb. 5	171	95	Siphon	Used solution			4124.61		Porous cup on anode end; short circuit
	172	93	do	do	2 hours	½ amp.	33.23		Siphon without porous cup
	173	27	Richards	do			31.24		
	174	28	do	do			27.77		Deposit spoiled
8	175	27	do	Frankfurt 10%			4097.39	1.11704	
	176	28	do	Used solution	7200.28	0.509438	97.09	695	Anode liquid
	177	125	do	Frankfurt 10%			97.38	703	
	178	126	do	Used solution			97.03	694	Do.
10	179	27	do	Frankfurt 10%			4098.69	1.11707	Not filtered
	180	28	do	Frankfurt 10% filtered	7202.50	0.509429	98.30	696	Pasteur filter No. 1 used
	181	125	do	Frankfurt 10%			98.74	708	Not filtered
	182	126	do	Frankfurt 10% filtered			98.23	694	Pasteur filter No. 1 used
12	183	95	Siphon	Frankfurt 10%			4105.75		Porous cup over anode end of siphon
	184	93	do	do	2 hours	½ amp.	05.63		Without porous cup
	185	27	Richards	do			05.04		
	186	28	do	do			05.05		
15	187	27	do	do			4097.42	1.11704	
	188	28	do	Used solution+added salt	7200.38	0.509432	97.43	704	Frankfort salt added to bring concentration to 10%
	189	125	do	do			97.34	702	
	190	126	do	Frankfurt 10%			97.10	696	Silver lost

17	191	27	.....do.....	Used+salt, filtered No. 2.....			4097.84	1.11702	Same electrolyte as No. 188 and 189 filtered through Pasteur filters No. 1 and No. 2 especially cleaned
	192	28	.....do.....	Used+salt, filtered No. 1.....	7200.71	0.509470	97.63	696	
	193	125	.....do.....	.....do.....			97.59	695	
	194	126	.....do.....	Used+salt, filtered No. 2.....			97.69	698	
19	195	27	.....do.....	Frankfurt 10% filtered.....			4098.68	1.11702	Electrolyte for two filtered through purified asbestos Filtered and unfiltered agree
	196	28	.....do.....	Frankfurt10% unfiltered.....	7202.76	0.509431	98.77	704	
	197	125	.....do.....	.....do.....			98.64	701	
	198	126	.....do.....	Frankfurt 10% filtered.....			98.69	702	
23	199	27	Rayleigh.....	Frankfurt 10%.....			4100.41	1.11746	One sheet of No. 595 paper
	200	28	Richards.....	.....do.....	7202.90	0.509432	4098.79	702	
	201	125	.....do.....	.....do.....			98.62	697	
	202	126	Rayleigh.....	.....do.....			4100.59	751	Do.
25	203	27	Richards.....	.....do.....			4098.46	1.11704	Neutral electrolyte
	204	28	.....do.....	.....do.....			98.33	701	Acid 1×10^{-5} present
	205	125	.....do.....	.....do.....			98.28	699	Do.
	206	126	.....do.....	.....do.....	7202.27	0.509427	98.15	696	Neutral electrolyte
	207	127	Poggendorff.....	.....do.....			98.35	701	Washed silk used
	208	128	.....do.....	.....do.....			98.56	707	Do.
Mar. 2	209	95	Siphon.....	.....do.....			4099.37	1.11756	In parallel both halves
	210	93	.....do.....	.....do.....			98.99		
	211	27	.....do.....	.....do.....	First half.		98.83	743	Do.
	212	125	.....do.....	.....do.....	7200.04	0.509422	98.56		
	213	126	Richards.....	.....do.....	Second half.		97.25	707	In first half only
	214	28	.....do.....	.....do.....	7200.54	0.509415	97.62	711	In second half only
	215	127	Poggendorff.....	.....do.....			97.26	707	In first half only; silk used
	216	128	.....do.....	.....do.....			97.72	713	In second half only; silk used
5	217	95	Siphon.....	.....do.....			8199.81	1.11774	Double siphon. In both halves
	218	127	Poggendorff.....	.....do.....	First half.		4097.52	712	With silk. In first half
	219	128	.....do.....	.....do.....	7200.20	0.509422	8195.93	721	With silk. In both halves
	220	28	Richards.....	.....do.....			4066.81	708	In parallel both halves
	221	125	.....do.....	.....do.....	Second half.		4128.14		
	222	126	.....do.....	.....do.....	7200.62	0.509417	4097.30	706	In first half only
	.....	27	.....do.....	.....do.....			.....	.....	Spoiled; deposit grew through porous cup

TABLE 1—Continued

General Table of Quantitative Results for 1910—Continued

Date	No.	Bowl	Form	Electrolyte	Time	Current	Deposit	Electro-chemical equivalent	Remarks
					sec.	amp.	mg.		
Mar. 9	223	95	Richards	Recrystallized Baker 10%			4097.79	1.11707	
	224	93	Poggendorff	Frankfurt 10%			98.10	715	With silk
	225	127	Richards	Recrystallized Baker 10%			97.92	710	
	226	128	Poggendorff	Frankfurt 10%	Second half.		98.28	720	Do.
	227	27	Rayleigh	do	7200.94	0.509426	98.27	720	Filter tube from PTR
	.....	126	Richards	do			.....	.....	Spoiled; accident in washing.
	228	125	Rayleigh	do			99.02	740	BS filter tube, not washed
	.....	28	Richards	do			.....	.....	Spoiled; deposit grew through porous cup
12	229	95	do	do			4098.83	1.11727	Cup water washed. Trace of alkali
	230	127	do	do			98.92	729	Do.
	231	27	do	do	7201.40	0.509432	98.38	714	Cup water washed
	232	28	do	do			98.87	728	Cup acid washed. Baked 700°
	233	125	do	do			98.26	711	Cup water washed
	234	126	do	do			98.19	709	Cup water washed. Baked 700°
16	235	127	Poggendorff	do			4098.28	1.11707	With silk
	236	128	do	Baker 10%			98.62	716	Do.
	237	27	Richards	Frankfurt 10%	7201.82	0.509424	98.69	718	At 50° C. Trace of alkali
	238	28	do	do			98.09	702	At room temperature
	239	125	do	Recrystallized Baker 10%			98.09	702	At 50° C.
	240	126	do	do			98.09	702	At room temperature

19	241	95	do	Frankfurt 10%	7201.17	0.509427	4097.96	1.11709	New cup, water washed. Trace alkaline
	242	93	do	do			97.94	709	Old cup, water washed. Trace alkaline
	243	127	do	do			97.63	700	New cup, water washed. Trace alkaline.
	244	128	do	do			97.65	701	Old cup, water washed. Trace alkaline
	245	27	do	do			97.22	689	Old cup, water washed. Baked, alkaline
	246	28	do	do			97.62	700	New cup, water washed. Trace alkaline
	247	125	do	do			97.27	690	Old cup, water washed. Trace alkaline
	248	126	do	do			97.38	693	New cup, acid washed. Baked, alkaline
23	249	95	do	do	7202.15	0.509422	4099.05	1.11723	
	250	93	do	Recrystallized Baker 10%			98.42	706	
	251	127	do	Frankfurt 10%			98.88	718	
	252	128	do	Recrystallized Baker 10%			98.32	703	
	253	27	do	Frankfurt 10%			98.69	713	At room temperature
	254	28	do	do			98.57	710	At 50° C
	255	125	do	Recrystallized Baker 10%			98.24	701	At room temperature
	256	126	do	do			98.11	698	At 50° C
26	257	95	do	Recrystallized Frankfurt 10%	2 hours	½ amp.	4098.84	.....	
	258	93	do	Recrystallized Baker 10%			98.96	.....	
	259	127	do	Recrystallized Frankfurt 10%			98.89	.....	
	260	128	do	Recrystallized Baker 10%			98.98	.....	
	261	27	do	Recrystallized Frankfurt 10%			98.62	.....	
	262	28	do	Recrystallized Baker. 10%			98.78	.....	
	263	125	Rayleigh	do			99.65	.....	PTR filter tube
	264	126	do	do			99.66	.....	BS filter tube washed

TABLE 1—Continued

General Table of Quantitative Results for 1910—Continued

Date	No.	Bowl	Form	Electrolyte	Time	Current	Deposit	Electro-chemical equivalent	Remarks
					sec.	amp.	mg.		
Mar. 31	265	95	Richards	Recrystallized Frankfurt 10%			4098.63	1.11704	
	266	93	do	Electrolyzed Frankfurt 10%			99.19	719	Spot in bowl on silver
	267	26	do	Baker 10%			98.91	711	
	268	127	do	Electrolyzed Baker 10%	Second half.		98.79	708	
	269	128	do	do	7202.78	0.509414	98.77	708	
	270	27	do	Electrolyzed Frankfurt 10%			98.51	701	
	271	28	do	Frankfurt 10%			98.71	706	
	272	125	do	Recrystallized Frankfurt 10%			98.42	698	
	273	126	do	Frankfurt 10%			98.70	706	
Apr. 5	274	27	do	Electrolyzed Frankfurt 10%			4099.61	1.11778	Experiment abnormal, due to probable contamination of electrolyte, deposits striated.
	275	28	do	Recrystallized Frankfurt 10%	7198.98	0.509474	4100.05	788	
	276	125	do	Frankfurt 10%			4099.96	785	
	277	126	do	Filtered Baker 10%			4098.10	725	

C. CLASSIFIED RESULTS

1. THE SMALL POROUS CUP VOLTAMETER

During this period of the work we found the small porous cup voltameter to be the most reliable and convenient form to use as a standard. It possesses important advantages in ease of manipulation, economy of materials, and reliability of results. Table 2 shows the results of 44 deposits made, using the four small voltameters. Two of these were gold and two platinum cups, all being of the same weight and capacity. The electrolyte was in most cases new, prepared from pure silver nitrate as purchased, without recrystallization. In all but four cases it was 10 per cent electrolyte, in two cases it was used solution brought up to 10 per cent by adding new salt, in a few cases it differed in other particulars, all of which are noted in the table.

The average value is 1.11703 mg per coulomb, as defined in Part I, page 190. This corresponds to a value of 1.01827_5 volts for the Weston Normal Cell at 20° C. The average variation of a single determination from the mean is 3 parts in 100 000, which we consider a satisfactory result, considering that variations in the measurement of time and current enter as well as appreciable variations in the electrolyte.

The deposits were uniform in character, white in color, always nonstriated, adherent, and crystalline as seen under the microscope. There is very little loose silver, and by the method of washing employed this is left in the cups, so that it is seldom necessary to return silver in appreciable quantity to the cups. We believed the silver nitrate to be very pure, but had at this time no sure criterion as to how near it was to absolute purity. Subsequent work with electrolytes conforming to the tests described in Section II of this paper has confirmed our belief in the accuracy of the results obtained, using the small porous cup voltameter.

TABLE 2

Summary of Results using Small Richards Voltameters, Second Series

Date	No.	Electro-chemical equivalent	Electrolyte	Remarks
1909				
Dec. 17	128	1.11698	15% Frankfurt $AgNO_3$	Coarse porous cup
	129	707	do	
	130	700	do	
	131	703	do	
1910				
Jan. 26	158	704	10% Frankfurt $AgNO_3$	
	159	709	do	
28	161	702	do	
	162	700	do	Filtered through bulb
	163	701	do	
	164	701	do	Do.
Feb. 8	175	704	do	
	177	703	do	
10	179	707	do	
	181	708	do	
15	187	704	do	
	188	704	do	Used+added salt
	189	702	do	Do.
	190	696	do	
19	195	702	do	Filtered through asbestos
	196	704	do	
	197	701	do	
	198	702	do	Do.
23	200	702	do	
	201	697	do	
25	203	704	do	
	204	701	do	A little acid present
	205	699	do	Do.
	206	696	do	
Mar. 2	213	707	do	
	214	711	do	
5	220, 221	708	do	2 in parallel, 4 hours
	222	706	do	
12	231	714	do	
	233	711	do	
16	238	702	do	
	240	702	do	Recrystallized $AgNO_3$
19	246	700	do	
	247	690	do	
23	253	713	do	
	255	701	10% Baker $AgNO_3$	Recrystallized
31	270	701	10% Frankfurt $AgNO_3$	Electrolyzed
	271	706	do	
	272	698	do	2 recrystallizations
	273	706	do	

Mean of 44=1.11703; mean variation= ±3.
Value for Weston Normal Cell=1.018275 at 20° C on present basis.[4]

[4] Circular of the Bureau of Standards, No. 29.

In order to show the reproducibility of the small porous cup voltameter, the weights of 54 deposits made in pairs (except two sets of three each), in which the electrolyte and other conditions were as nearly identical as possible in the two cups of each pair, have been tabulated. The following paragraph, written two years ago, still represents our views concerning the possibilities of this type of voltameter:

The average deviation of each value from the mean of each group of two or three is only *one part in one hundred thousand.* That is, when the variations in the measurement of current and time are eliminated and the variation in the electrolyte is removed, so that it is simply a question of how nearly two similar voltameters agree with one another, and the variation is that produced by the loss of silver, fluctuation in moisture or impurity in the deposit, and the error of weighing the cups before and after the deposit, the average deviation of a cup from the mean of a pair is only one-thousandth of 1 per cent, the deposit being 4 grams and the number of deposits 54, extending through a period of three months. If the single deposits agree so closely and the average deviation from the mean of 44 deposits is only 3 parts in 100 000, it is evident that the small porous cup voltameter, as we have used it, is an instrument of high precision and capable of serving as a means of checking the constancy of the Weston Normal Cell, as the London Conference has declared it must be employed to do, *provided* there is no uncertainty in its use which we have not discovered, and that it is possible to obtain silver nitrate of so uniform purity that no appreciable variation in value will occur in future use due to changes in the degree of purity of salt employed.

TABLE 3

Showing the Reproducibility of the Small Porous Cup Voltameter

[The deposits made under the same conditions are arranged in groups. In column Δ are tabulated the differences of each member of the group from the group mean. The average of these differences for 54 deposits is 0.04 mg or 1 part in 100 000 of the deposit.]

Date	No.	Deposit	Mean	Δ
1909		mg.	mg.	mg.
Dec. 17	128	4096.93		0.07
	130	6.98	4097.00	.02
	131	7.10		.10
1910				
Jan. 7	138	8.04		.00
	140	8.10	8.04	.06
	141	7.97		.07
13	145	6.34	6.34	.00
	146	6.34		.00

TABLE 3—Continued

Showing the Reproducibility of the Small Porous Cup Voltameter—Contd.

Date	No.	Deposit	Mean	Δ
1910		mg.	mg.	mg.
Jan. 26	158	4097.41	7.48	.07
	159	7.56		.08
	157	6.78	6.84	.06
	160	6.91		.07
28	161	6.97	6.95	.02
	163	6.94		.01
	162	6.89	6.91	.02
	164	6.93		.02
31	165	3.51	3.53	.02
	166	3.55		.02
Feb. 3	167	0.93	0.94	.01
	170	0.95		.01
	168	0.89	0.86	.03
	169	0.84		.02
8	175	7.39	7.38	.01
	177	7.38		.00
	176	7.09	7.06	.03
	178	7.03		.03
10	179	8.69	8.72	.03
	181	8.74		.02
	180	8.30	8.26	.04
	182	8.23		.03
12	185	5.04	5.05	.01
	186	5.05		.00
15	187	7.42	7.25	.16
	190	7.10		.16
	188	7.43	7.38	.05
	189	7.34		.04
17	191	7.84	7.77	.07
	194	7.69		.08
	192	7.63	7.61	.02
	193	7.59		.02

TABLE 3—Continued

Showing the Reproducibility of the Small Porous Cup Voltameter—Contd.

Date	No.	Deposit	Mean	Δ
1910		mg.	mg.	mg.
Feb. 19	195	4098.68	8.68	.00
	198	8.69		.01
	196	8.77	8.70	.07
	197	8.64		.06
23	200	8.79	8.70	.09
	201	8.62		.08
25	203	8.46	8.30	.16
	206	8.15		.15
	204	8.33	8.30	.03
	205	8.28		.02
Mar. 12	231	8.38	8.32	.06
	233	8.26		.06
31	271	8.71	8.70	.01
	273	8.70		.00
			Average...	.04

2. THE LARGE POROUS CUP VOLTAMETER

Table 4 gives the results of 28 deposits in the large and medium cups, using 10 per cent Frankfurt electrolyte mostly, but with a few deposits from Baker, new or recrystallized, or electrolyzed, and a few from Frankfurt used and recrystallized. The mean value for all is 1.11710, or omitting two deposits, Nos. 229 and 230, 1.11709, with an average variation from the mean of 4 parts in 100 000, not quite as uniform agreement as with the small cups, but it will be noticed that there are a good many varying conditions.

TABLE 4

Deposits in Large and Medium Size Richards Voltameters

Date	No.	Size	Electro-chemical equivalent	Porous cup	Electrolyte
1909					
Dec. 17	122	l.	1.11705	Large porous cup.....	15% Frankfurt $AgNO_3$
	124	l.	711	.....do.....	10% Frankfurt $AgNO_3$
	125	m.	701	.....do.....	Do.
1910					
Jan. 7	135	m.	708	.....do.....	10% Baker
13	144	l.	709	.....do.....	10% Frankfurt
21	149	l.	714	Small porous cup.....	7.5% used Frankfurt
	150	m.	712	Large porous cup.....	10% new Frankfurt
Mar. 9	223	l.	707	Small porous cup.....	10% Baker, twice recrystallized
	225	m.	710	.....do.....	Do.
12	229	l.	727	Small, trace of alkali	10% Frankfurt
	230	m.	729		
19	241	l.	709	Small new cup.....	Do.
	242	l.	709	Small old cup.....	Do.
	243	m.	700	Small new cup.....	Do.
	244	m.	701	Small old cup.....	Do.
23	249	l.	723	Small porous cup	Do.
	250	l.	706	.....do.....	10% Baker recrystallized
	251	m.	718	.....do.....	Frankfurt
	252	m.	703	.....do.....	Baker recrystallized
26	257	l.	706	.....do.....	10% Frankfurt recrystallized
	258	l.	709	.....do.....	10% Baker recrystallized
	259	m.	708	.....do.....	10% Frankfurt recrystallized
	260	m.	710	.....do.....	10% Baker recrystallized
31	265	l.	704	.....	10% Frankfurt recrystallized
	266	l.	719	.....	10% Frankfurt electrolyzed
	267	m.	711	.....	10% Baker
	268	m.	708	.....	10% Baker electrolyzed
	269	m.	708	.....	Do.

Mean of 28 deposits=1.11710
Mean of 26 deposits=1.11709, omitting (229 and 230) $\pm 4/10^5$
Mean of 18 deposits=1.11708, omitting 8 relative deposits
The value 1.11709 corresponds to 1.01833 volts for the Weston Normal Cell at 20° C, assuming the electrochemical equivalent of silver to be 1.11800 mg per coulomb, as explained on page 190. This is 6 in 100 000 larger than the mean of 44 deposits in small cups. We regard this difference of 6 in 100 000 as of particular significance and discuss it at length on page 514.

3. POGGENDORFF VOLTAMETER

Table 5 gives the results of 17 deposits in the Poggendorff voltameter, the first 7 having been made without silk or any septum, and the last 10 with pure raw silk that had been thoroughly washed with hot distilled water. In the first 3 the deposits were much too heavy, but the next 4 were about

normal for the kinds of electrolyte used. In the later deposits, using washed silk, the deposits average 1.11712, or omitting No. 219 of a four-hour run, which gave a high value and No. 236 made with less pure salt, the average is 1.11710. This is nearly in agreement with the porous cup voltameter, which for this size of voltameter ought to average about 1.11706. The difference is too small to be sure of, unless more deposits are made under identical conditions.

TABLE 5

Summary of Deposits in the Poggendorff Voltameters

Date	No.	Size	Electrochemical equivalent	Septum	Electrolyte
1909					
Dec. 17	123	l.	1.11849	No silk.....	15% Frankfurt salt
	126	m.	733	.....do.....	Do.
	127	m.	738	.....do.....	Do.
1910					
Jan. 7	136	m.	710	.....do.....	10% Baker
	137	m.	709	.....do.....	Do.
21	151	m.	708	.....do.....	Used electrolyte filtered through porous cup
	152	m.	707	.....do.....	New electrolyte filtered through porous cup
Feb. 25	207	m.	701	Washed silk.....	10% Frankfurt
	208	m.	707	.....do.....	Do.
Mar. 2	215	m.	707	.....do.....	Do.
	216	m.	713	.....do.....	Do.
5	218	m.	712	.....do.....	Do.
	219	m.	721	.....do.....	Do.
9	224	m.	715	.....do.....	Do.
	226	m.	720	.....do.....	Do.
16	235	m.	707	.....do.....	Do.
	236	m.	716	.....do.....	10% Baker

Mean of last 10=1.11712
Mean of last 10=1.11710 (excluding 219 and 236)
The mean is very nearly the same as that found with large and medium porous cup voltameters, being 1.11710 as compared with 1.11709. The value of 1.11710 mg per coulomb corresponds to 1.01834 volts for the Weston Normal Cell at 20° C, assuming the electrochemical equivalent of silver to be 1.11800 mg per coulomb as fixed by the London Conference of 1908.

4. SIPHON VOLTAMETER

The siphon form of voltameter has been employed by some observers as a test for the reliability of other forms. We therefore made some study of its performance under varying conditions. We have made 11 deposits altogether in the siphon form of voltameter, using both large and small cups and large and

small glass siphons (see our first paper, p. 174). The runs are relative, but have always been compared with the Richards form of voltameter, and from the assumed values of the latter the electrochemical equivalent of the siphon form is found.

TABLE 6

Results with the Siphon Voltameters

Date	No.	Electrolyte	Electrochemical equivalent	Remarks
1910				
Jan. 7	133	Baker 10%	1.11740	Large bowl
	134	.....do	740	Do.
13	142	Frankfurt 10%	726	Do.
	143	.....do	727	Do.
21	147	Used Frankfurt	720	Do.
	148	.....do	707	Porous cup over cathode end
Feb. 12	183	Frankfurt 10%	720	Porous cup over anode end
	184	.....do	717	Large bowl
Mar. 2	209	.....do	756	2 large bowls in parallel
	210	.....do		
	211	.....do	743	2 small bowls in parallel
	212	.....do		
5	217	.....do	774	2 siphons in 1 large bowl

Mean, 1.11736.
The corresponding value for the Weston Normal Cell at 20° is 1.01858.

The first two deposits (Nos. 133 and 134), using Baker $AgNO_3$, agree with one another, giving 1.11740. The next two, January 13, with Frankfurt $AgNO_3$, somewhat purer, give lower values, 1.11726 and 1.11727. In the third trial, January 21, with a used solution we obtained 1.11720 and 1.11707, but in the latter *a porous cup was placed over the cathode end of the siphon and was therefore equivalent to a Richards voltameter*. In the fourth trial, February 12, the values were nearly alike, 1.11720 and 1.11717, the first having a porous cup over the anode end. It was therefore equivalent to a Richards voltameter of very large volume. In the fifth trial, March 2, there were two large siphon voltameters in parallel, equivalent to one of double volume, and the current was one-fourth ampere in each for four hours. The value is very high, 1.11756. There were also two smaller siphons in parallel,

using small cups. They gave 1.11743, still a large value. In the sixth trial we employed two large siphons dipping into one large platinum dish, with two anodes in parallel. An 8-gram deposit was made, giving 1.11774, the largest of all. We thus have 10 deposits (excluding No. 148, which was a Richards of usual volume), which gives a mean value of 1.11736, about 30 parts in 100 000 greater than the small-size Richards voltameter. The values vary greatly with the volume of the electrolyte. We thought it possible that if the $AgNO_3$ were perfectly pure the different sizes would give the same values and that they would be correct. We have later found this to be true. But the variation of the results in our experience is so large and they are so awkward to use that we have seldom used them since.

5. FILTER PAPER VOLTAMETER

We made very few experiments with this form of voltameter, owing to the errors shown to exist in it by the results of the first series of experiments. The few determinations recorded here were for the purpose of trying out special features.

Table 7 gives the results of seven deposits, using filter paper. The first deposit (No. 132) was made with a smaller quantity of the filter paper immersed in the electrolyte than usual, more nearly as Mr. Smith has done in his work. The deposit nearly agrees with his value. Nos. 199 and 202 corresponded to the earlier arrangement and give about the same values as we then obtained. The next two deposits give a comparison of two filter tubes, one of which was received from the Reichsanstalt and the other was from our own stock, but like the first, except that it had not been washed previous to use. The latter gave a much heavier deposit. Accordingly, we made two other deposits (Nos. 263 and 264), in which we washed our filter tube thoroughly and treated it with dilute alkali, and then washed again with distilled water. The alkali dissolves out in considerable degree the furfural-yielding carbohydrates. The deposits with the Reichsanstalt tube and our own then agreed exactly, but both are considerably heavier than with porous cup voltameter.

Chemical tests show that while this special treatment of filter paper makes it less readily decomposed into furfuraldehyde, the

filter paper thus treated never becomes entirely resistant, and hence the deposit will always be abnormally large.

TABLE 7

Summary of seven deposits in Filter Paper Voltameter

Date	No.	Electro-chemical equivalent	Filter paper	Electrolyte
1910				
Jan. 7	132	1.11723	Small quantity of filter paper	10 % Baker salt
Feb. 23	199	746	1 sheet filter paper	10 % Frankfurt
	202	751	.....do	Do.
Mar. 9	227	720	Small filter tube from PTR	Do.
	228	740	Small filter tube from BS	Do.
26	263	726	Small filter tube from PTR	10 % Baker recrystallized
	264	726	Small filter tube from BS washed	Do.

Mean of 7=1.11733.

The corresponding value for the Weston Normal Cell at 20° is therefore 1.01855 volts.

D. SPECIAL QUESTIONS

1. USED SOLUTIONS

In connection with the first series of experiments, some discussion has been given of the effects observed when an electrolyte is used in the voltameter for the second or third time. The fact has been noted that used solutions free from filter paper or other contamination give normal or slightly smaller deposits than the same solution unused. In the case of electrolytes containing traces of impurities, such as those made from the salt as generally purchased, the lower deposit may be due in part at least to the purifying effect of previous electrolysis.

As a rigid test of this, we have successively electrolyzed a solution of silver nitrate which was strongly contaminated with filter paper until it gave a deposit of well-formed crystals free from striations. The electrolyte was 15 per cent $AgNO_3$, which had stood in contact with filter paper for several months. It was electrolyzed in a small voltameter at normal current density, but without septum between the anode and cathode in order to maintain the concentration of the electrolyte. As might be expected, the first deposit was strongly striated and leaden colored. This

deposit was removed and the electrolysis begun again. The second, third, and fourth deposits were all strongly striated and not crystalline. The fifth deposit was also striated, but a few crystal faces were to be seen. These increased in number in the succeeding sixth, seventh, eighth, and ninth deposits, and at the same time the striations were becoming less and less prominent. In the tenth deposit the striations completely disappeared and the crystalline structure was good. This matter seemed so important that we made several similar experiments to confirm it. In these we successively electrolyzed solutions contaminated with filter paper and others with meta-furfuraldehyde. The result was the same in all cases. We found the impurities could be eliminated by sufficiently prolonged electrolysis. We shall refer to this phenomenon again in discussing the "volume effect" on page 514.

During the present series of quantitative experiments we have employed used solutions in the runs of January 21, February 5, 8, 15, 17, March 31, and April 5. The experiments of February 8, 15, and March 31 were made expressly to test the effect of previous electrolysis. In the others, except the abnormal experiment of April 5, we introduced other variations. In the first of these three we used a clear anode solution saved from the Richards voltameter of previous experiments. Two deposits were made from this electrolyte in the small voltameters and compared with two similar deposits from our 10 per cent Frankfurt salt. The results are as follows:

Anode liquid		Frankfurt electrolyte	
No. 176	1.11695	No. 175	1.11704
No. 178	1.11694	No. 177	1.11703

Deposit from anode liquid is less by 8 parts in 100 000.

In the experiment of February 15 we compared the cathode liquid (from the Richards voltameter) to which we added enough Frankfurt crystallized salt to bring the concentration up to 10 per cent with a 10 per cent new solution of the Frankfurt electrolyte and found the two in good agreement.

Used+added salt		Frankfurt electrolyte	
No. 188	1.11704	No. 187	1.11704
No. 189	1.11702	No. 190	1.11696

No. 190 probably abnormally low, owing to accident.

It thus appears that used solutions yield normal results if some fresh salt is added to keep up the concentration of the electrolyte.

On March 31 we compared our Baker and Frankfurt salt with recrystallized and electrolyzed samples. Except for No. 266, which was abnormally heavy owing to a spot found on the silver deposit when the bowl was weighed, the results show that the values for the electrochemical equivalent from the recrystallized and elctrolyzed samples are lower than from the original salt.

TABLE 8

No.	Size	Original salt		Electrolyzed		Recrystallized Frankfurt
		Baker	Frankfurt	Baker	Frankfurt	
265	l.	.....	.....	.....	.....	1.11704
266	l.	.....	.....	.....	(1.11719)	.....
267	m.	1.11711	.....	.....	.....	.....
268	m.	.....	.....	1.11708	.....	.....
269	m.	.....	.....	1.11708	.....	.....
270	s.	.....	.....	.....	1.11701	.....
271	s.	.....	1.11706	.....	.....	.....
272	s.	.....	.....	.....	.....	1.11698
273	s.	.....	1.11706	.....	.....	.....
Means		1.11711	1.11706	1.11708	1.11701	1.11701

The significance of these figures will be brought out in the next section.

2. VOLUME EFFECT

By comparing the results of the two sizes of porous cup voltameters (Tables 2 and 4) it will readily be seen that the deposits in the large size are with few exceptions heavier than in the small voltameters. The difference amounts to about 7 parts in 100 000. This phenomena we have called the *volume effect.* In these experiments the volume of electrolyte in the large voltameters was about three times that in the small voltameters. We find evidence of this volume effect in the work of Lord Rayleigh and Mrs.

Sedgwick.[5] Employing voltameters with a greater disparity in volume the effect is made still more apparent. This is shown in our results with the siphon voltameter and is in accord with the observations of Laporte and de la Gorce.[6]

Since we regard this matter of the volume effect as of considerable importance we shall state rather fully the evidence for believing in its reality and our theory as to its probable cause and the means of avoiding it.

During the earlier part of the work when using the largest size of porous pots in the large-size platinum bowls the volume of the cathode liquid was but little greater than that in the small voltameters. The resulting disparity in the deposits being therefore small was usually attributed to experimental error. But when using the small-size porous cups in the large voltameters, with a larger volume of the cathode liquid, the difference became more apparent. On making an examination of the records it appeared that the large voltameters in practically every case contained heavier deposits than the smaller sizes. By taking the two voltameters in pairs, identical in all respects except the volume of the electrolyte, we were forced to conclude that the observed difference is a function of the volume.

Judging the electrolyte used in these runs by present standards of purity, we find them to have been far from absolutely pure. This suggests the probable cause for the volume effect and is supported by the following evidence. In the curves shown in figures 1 and 2 the slope of the lines is a measure of the volume effect. The steeper curve represents the volume effect of the electrolyte as purchased, while the more nearly horizontal line represents the volume effect of the same salt after purification by electrolysis in the voltameter or by recrystallization. With an electrolyte of sufficient purity all sizes of voltameters should give the same weight of deposit, provided the volume is the only variable. In our latest work we have attained such a degree of purity of the electrolyte that the volume effect vanishes.

As before stated, we place greater reliance on determinations with the small porous cup voltameter with solutions not quite pure

[5] Phil. Trans., 175, p. 411; 1884. [6] Bull. Soc. Int. Electr., March, 1910.

than on any other form. The reason for this is that with so small a volume the effect of the impurities is very much less than for the greater volumes. This is shown by the wide divergence of the above curves of figures 1 and 2 for volumes of 200 cc or over.

In the case of the porous cup voltameter the volume of electrolyte considered is that of the cathode chamber only and not the total volume of liquid in the voltameter; this conclusion is justified by the following observations:

TABLE 9

Date	No.	Form	Total volume of electrolyte	Volume of cathode liquid	Deposit
1910			cc		mg
Jan. 21	147	Siphon	500	.....	4149.11
	148	Siphon, porous cup over cathode end	500	210	4148.58
	149	Richards	340	320	4148.86
	153	.....do	115	90	4148.47
Feb. 12	184	Siphon	500	.....	4105.63
	183	Siphon, porous cup over anode end	500	450	4105.75
	185	Richards	115	90	4105.04
	186	.....do	115	90	4105.05

These results show that when the porous cup is over the anode end of the siphon the weight of deposit is substantially the same as for the siphon voltameter without any septum, while for the case of the pot over the cathode end the volume of liquid contained inside of it and the siphon is without effect.

The cause of this effect we believe to be the presence of reducing impurities and consequent colloidal silver in the electrolyte. Solutions showing the volume effect can be shown to be impure by a test with potassium permanganate as described on page 531. Since the colloidal silver can not pass through the porous pot, it is only the volume of the cathode liquid that should be effective in increasing the deposit, which is in accord with experimental data. Impurities which are not sufficient to cause striations may be sufficient to produce a small volume effect, and *therefore we may use this as a more rigid criterion by which to judge the purity of the electrolyte than the appearance of the deposit.*

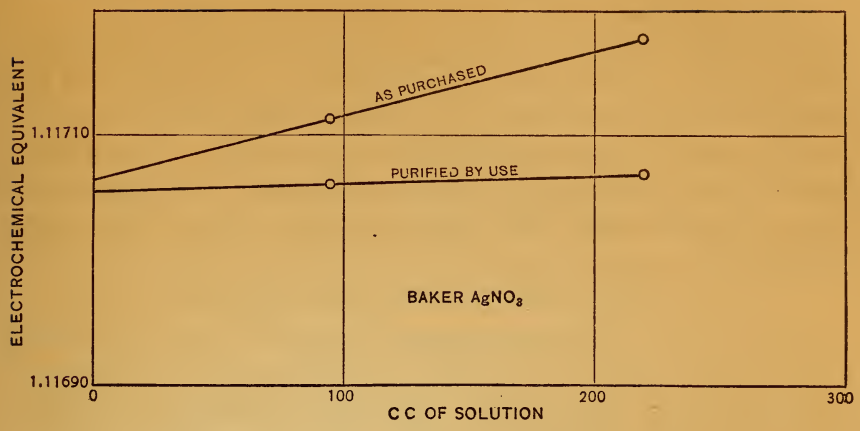

Fig. 1.

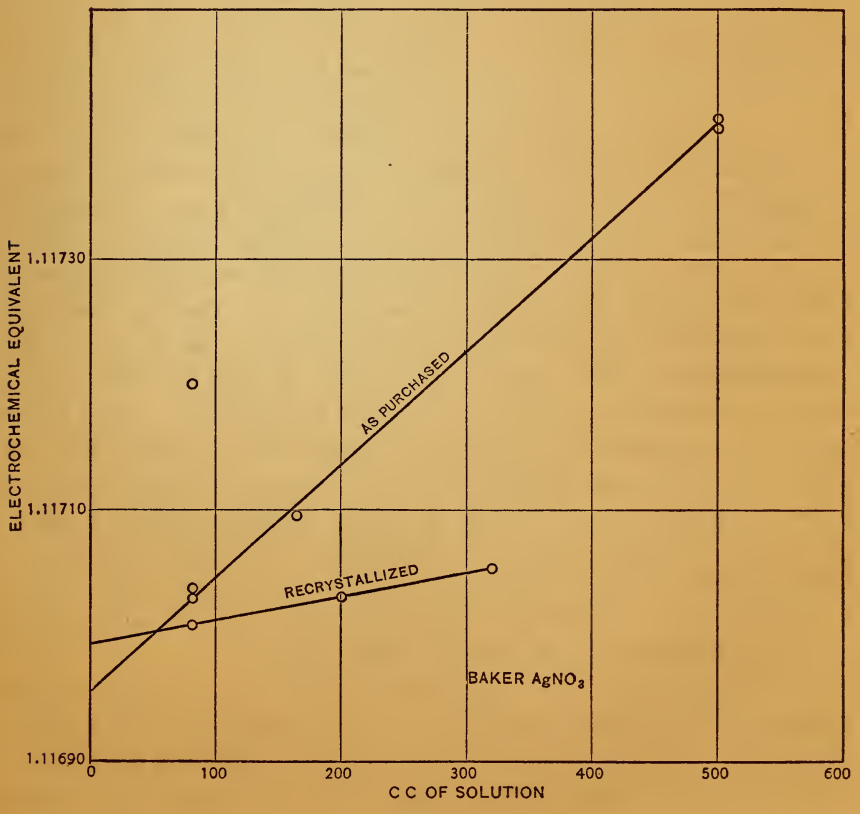

Fig. 2.

Figs. 1 and 2.—*Effect of purification of the $AgNO_3$ on the volume effect which is represented by the slope of the curves.*

With a relatively small volume of electrolyte the quantity of colloidal silver deposited during a given time is less than with a larger volume. Gradually the colloidal silver is deposited out and the electrolyte becomes purer, and hence a used solution may give a more nearly normal value than a new solution. Hence, with solutions not quite pure we see why the smaller voltameters give more consistent and more nearly correct values than larger voltameters.

3. ANODE SLIME IN THE POGGENDORFF FORM

The cause of the wide variations in the results of the Poggendorff or nonseptum form of voltameter we attributed to the difficulty of confining the anode slime. The results tabulated in Table 5 show an average variation from the mean of 9 parts in 100 000, which is an unfavorable showing as compared with our results on the porous cup voltameter. The first seven of the deposits in the table show a larger mean variation than the average given above, and this is almost entirely due to anode slime becoming mixed with the deposited silver. Small bubbles of gas liberated by the warming of the electrolyte or from other causes carry small masses of slime to the surface of the liquid. When the gas is discharged the slime falls back, sometimes upon the cathode. We have investigated various means of separating it from the crystalline deposit, but have found no process that is satisfactory. The best perhaps is by stirring the liquid when the finely divided slime is carried in suspension for a short time by the liquid, leaving the larger particles of crystalline silver in the bottom of the dish. Some have effected the separation by means of a glass rod or feather, but we believe that this calls unduly upon the judgment of the observer, and we fail to find in such cases as small a variation from the mean as we believe may reasonably be expected. To avoid the trouble with slime we covered the anode with silk, but this is not satisfactory, because the silk is an active agent in the voltameter playing a somewhat similar rôle to filter paper.

Our results have confirmed those of Mr. F. E. Smith, who found that the trouble with slime from the anode may be greatly reduced by using electrolytic anodes with as large an active surface as possible. Such anodes possess the advantage of providing

silver of a high degree of purity and of an even hardness. The advantages of the former are apparent, while the latter tends to reduce the slime. We have observed with anodes of pure silver that have been rolled or sawed that a disintegration takes place under the surface, causing considerable pieces of it to fall off, accompanied by much black slime. This appears to depend upon the surface hardness of the metal. With anodes sufficiently covered with pure electrolytic silver the wearing away of the surface is uniform, and only a small quantity of gray slime appears.

4. FILTERING THE ELECTROLYTE

In May, 1909, we arranged to use a porous cup as a filter, employing the vacuum to hasten the process. It was first used in the experiment of May 6 and occasionally thereafter. We were not able to detect any change in the mass of deposit due to its use. The question was again taken up in the work of 1910, during which time we tried two Pasteur filters, designated as No. 1 and No. 2, and a little bulb of Pukal ware.

These were carefully cleaned before use. The results are given in Table 10. In making these tests we always used four small porous cup voltameters, two of which contained the filtered solution and two the same electrolyte not filtered.

Filter No. 1, which was used first, showed a surprising reduction of 15 parts in 100 000 in the deposit. We repeated this experiment, using the Pukal bulb, which caused no change in the deposit. Using filter No. 1 in a subsequent experiment we again found a reduction in the deposit amounting to 13 parts in 100 000. We then filtered one portion of electrolyte through filter No. 1 and another portion through an identically similar filter No. 2, which had not been acid cleaned. The deposit from the first gave a deposit 5 in 100 000 lower than the other, but this difference may have been due to a trace of alkalinity persisting in filter No 2, since it was not cleaned with acid. While it appeared that the Pukal bulb, like the porous pot previously used, was reliable as a filter, the contradictory evidence of the Pasteur filters led us to try purified asbestos as a filter with satisfactory results. The asbestos can be quickly prepared and expeditiously used. In our subsequent work we preferred to use it when it was neces-

sary to use a filter of any kind. In using either the asbestos or the Pukal filter it is best to discard the first portion of filtrate, owing to the tendency for acid to form before equilibrium is established between the solution and the filter.

TABLE 10

Showing the Effect of Filters on the Electrolyte

Date	No.	Electro-chemical equivalent	Remarks
1910			
Jan. 26	157	1.11687	Electrolyte filtered through filter No. 1
	160	691	Do.
	158	704	Electrolyte not filtered
	159	709	Do.
28	162	700	Electrolyte filtered through bulb
	164	701	Do.
	161	702	Electrolyte not filtered
	163	701	Do.
Feb. 10	180	696	Electrolyte filtered through filter No. 1
	182	694	Do.
	179	707	Electrolyte not filtered
	181	708	Do.
17	192	696	Electrolyte filtered through filter No. 1
	193	695	Do.
	191	702	Electrolyte filtered through filter No. 2
	194	698	Do.
19	195	702	Electrolyte filtered through asbestos
	198	702	Do.
	196	704	Electrolyte not filtered
	197	701	Do.

5. TEMPERATURE COEFFICIENT OF THE VOLTAMETER

Two tests of the effect of temperature on the mass of deposit were made, using in each case the four small voltameters, two of which were maintained at about 50° during the course of the experiment by heating coils wound on asbestos forms and made to fit closely about the platinum crucible. The temperature of each was obtained from thermometers standing in the porous cup of each voltameter. The temperatures were read every 10 minutes. The following curve shows them plotted against time for the second experiment (fig. 3):

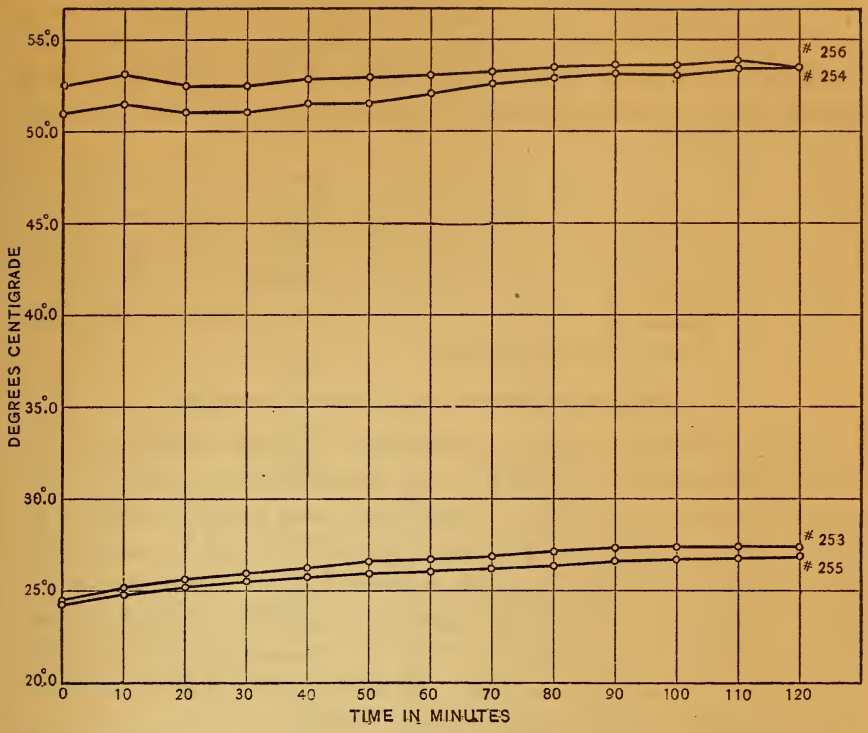

Fig. 3.—*Record of temperatures of four voltameters during the second experiment to determine the temperature coefficient.*

The results are contained in Table 11.

TABLE 11

Experiments on Temperature Coefficient

[The deposits in Nos. 256 and 255 are lower than Nos. 254 and 253 because the electrolyte was made from purer salt]

Date	No.	Electro-chemical equivalent	Remarks
1910			
Mar. 16	237	1.11718	Heated to 51° C (average)
	239	702	Heated to 55° C (average)
	238	702	Not heated, 23° C (average)
	240	702	Do.
23	254	710	Heated to 52° C (average)
	256	698	Heated to 53° C (average)
	253	713	Not heated, 26° C (average)
	255	701	Do.

In the first run the heated voltameters showed an average of 9 parts in 100 000 greater deposit, the difference of temperature being 29.5°, while the second experiment showed 3 parts in 100 000 smaller deposit in the heated voltameters, the difference in temperature being 26.5°.

The differences are probably due to experimental error, particularly in the case of No. 237, in which a trace of alkali was found after the experiment. The temperature coefficient deduced from these experiments is not more than one or possibly two parts in a million per degree and is more likely zero for perfectly pure solutions as it should be theoretically.

6. COMPARISON OF GOLD AND PLATINUM CATHODES

In the summer of 1909 we purchased two gold crucibles of the same dimensions and weight as the two platinum dishes, which we had found very useful. These four were usually arranged in pairs of one gold dish and platinum dish, each so that by tabulating the differences in deposit of the two crucibles of a pair we have a direct comparison of gold and platinum cathodes. This has been done in Table 12 for all cases where the material of the cathode was the only variation in the voltameter except for obviously abnormal determinations on January 7 and 21.

The result is to show a lighter deposit in the gold dishes by 1.4 parts in 100 000. This difference is less than the average variation from the mean of our most reliable determinations of the electrochemical equivalent and we regard it, therefore, as indicating the substantial agreement of the two materials.

TABLE 12

Comparison of Gold and Platinum Cathodes

Date	Gold dish	Platinum dish	Difference (parts in 10^5)
1909			
Sept. 9	4097.99	4098.21	−5.4
Dec. 17	4096.98	4096.93	+1.2
	4097.10	4097.27	−4.1
1910			
Jan. 7	4098.10	4098.04	0.0
	4097.97		

TABLE 12—Continued

Comparison of Gold and Platinum Cathodes—Continued

Date	Gold dish	Platinum dish	Difference (parts in 10^5)
1910			
Jan. 26	4096.91	4096.78	+3.2
	4097.56	4097.41	+3.7
28	4096.94	4096.97	−0.7
	4096.93	4096.89	+1.0
31	4163.55	4163.51	+1.0
Feb. 3	4130.84	4130.89	−1.2
	4130.95	4130.93	+0.5
8	4097.38	4097.39	−0.2
	4097.03	4097.09	−1.7
10	4098.74	4098.69	+1.2
	4098.23	4098.30	−1.7
15	4097.34	4097.43	−2.2
	4097.10	4097.42	−7.8
17	4097.69	4097.84	−3.7
	4097.59	4097.63	−1.0
19	4098.64	4098.77	−4.1
	4098.69	4098.68	+0.2
23	4100.59	4100.41	+4.4
	4098.62	4098.79	−4.1
25	4098.28	4098.33	−1.2
	4098.15	4098.46	−7.8
Mar. 2	4097.25	4097.62	−9.3
16	4098.09	4098.09	0.0
	4098.09	.....	.....
31	4098.70	4098.71	−0.2
	4098.42	4098.51	−2.2
		Average	−1.4

Deposit on gold lighter by 1.4 in 10^5.

These results answer the objections of Hering [7] to the use of platinum as the cathode in the voltameter. According to his theory the deposit in the gold crucibles should be the heavier, owing to the reduction of oxygen in the surface of the platinum. In another place we have noted the change in size of the silver crystals, due to saturating the surface of a strip of platinum with oxygen, but the effect on the mass of deposit seems to be negligibly

[7] Trans. Am. Elec. Chem. Soc., 12, p. 293.

small. Aside from the lower price of gold than platinum, we prefer the latter because of its being more durable.

The quantitative work on the second series of experiments was discontinued April 5, 1910, to take part in the cooperative work with the National Physical Laboratory, Physikalisch-Technische Reichsanstalt, and the Laboratoire Central d'Électricité.

II. PREPARATION AND TESTING OF SILVER NITRATE FOR USE IN THE SILVER VOLTAMETER

A. PRELIMINARY WORK WITH COMMERCIALLY PURE SILVER NITRATE

It was early found that the essential differences between the various types of voltameters, especially as regards the different character of septa employed, gave rise to variations in the values obtained, which were independent of the source of the silver nitrate used and which were far greater in magnitude than those arising from the relatively slight amounts of impurities present in commercially pure salt. Consequently no special attempt was made in this part of the work to obtain silver nitrate of the highest degree of purity such as was used later.

Two large lots of silver nitrate crystals obtained from the Gold- und Silber-Scheide-Anstalt, Frankfurt a. M., yielded silver deposits, when electrolyzed, which were nonstriated and markedly crystalline in character, and solutions of this salt in the best twice-distilled water were neutral toward litmus paper as nearly as could be judged.[8] This material was therefore used without further purification in many of the experiments recorded in the present paper. The values obtained with this salt, especially in the small Richards voltameter, are very near the true value, being in good agreement with the later results obtained with recrystallized salt of a very high degree of purity.

B. IMPORTANCE OF CERTAIN CLASSES OF IMPURITIES IN VOLTAMETER WORK

Our earlier investigations of the chemical problems connected with the voltameter had been confined almost entirely to the question of the effect of filter paper, and had revealed the pre-

[8] See p. 527.

ponderating importance of certain classes of reducing substances as impurities in the electrolyte. The pronounced effects produced in the voltameter by the presence of minute quantities (0.0001 per cent) of certain reducing substances had made it evident that no sample of silver nitrate, however carefully prepared, could be considered suitable for use in voltameter work of the highest precision without being actually tested for these exceedingly slight traces of reducing impurities. Amounts so small may be produced in ways which can not be prevented merely by excluding foreign organic material, because these impurities may be produced by the process of purification itself, as will be shown later. In this connection it must be borne in mind that these reducing impurities are not necessarily of organic origin, but may be formed from pure silver, nitric acid, and water (e. g., hydrazine, hydroxylamine, nitrites, hyponitrites, etc.), or colloidal silver itself may be formed directly from perfectly pure materials by heat or other conditions imposed by the nature of the process.

The above considerations hold true in the main of a few other impurities which affect the results in the voltameter, when present in small amounts. This applies especially to colloidal silver hydroxide, which the later work showed could have a pronounced effect upon the weight of the silver deposit when present to the extent of only a few parts per million. Very small amounts of free nitric acid also affect the results, but to a less extent than does the colloidal silver hydroxide. Other impurities which affect the results when present in small amounts are silica and carbon dioxide. These impurities are more easily excluded than the ones just mentioned, however, and relatively larger amounts are required to affect the results. Their influence will be discussed in a subsequent paper of this series.

By far the most difficult problems connected with the preparation of silver nitrate for use in the voltameter have to do with the exclusion or removal of reducing impurities (especially colloidal silver [9]) on the one hand and of "uncombined" acid or base on the other. It was found necessary, therefore, to carefully test all samples of material, however carefully prepared, for these objec-

[9] See p. 531.

tionable impurities. The tests employed for this purpose are discussed in the following pages. Methods of purification were finally devised, by means of which these impurities can be excluded with comparative ease, so that it is now a practicable matter to prepare silver nitrate of satisfactory purity for voltameter work.

C. TESTS FOR UNCOMBINED ACID AND BASE

1. NECESSARY CONDITIONS FOR THE TEST

It was found necessary, in order to obtain results of the accuracy desired in the voltameter determinations, to define the neutrality of the electrolyte to within a part in a million of "uncombined" acid or base. In this section an account will be given of the method that was developed to meet this requirement.

The test is not designed to determine the absolute concentration of the hydrogen ions, but only to determine whether there is any "excess" or "uncombined" acid or base present. Pure silver nitrate appears to be hydrolyzed to an appreciable extent, as indicated by its behavior toward methyl orange, phenolphthalein, and some other indicators (see Part II, p. 247) and by certain other properties. A brief theoretical discussion of the degree of hydrolysis of this salt in $\frac{N}{2}$ solution is given below.[10] The question as

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[10] The theoretical degree of hydrolysis of $\frac{N}{2}$ $AgNO_3$ may be calculated from the solubility products of AgOH and H_2O. For—

$$\frac{\alpha^2}{(1-\alpha)V}=\frac{k_w}{k_b}$$

where α = degree of hydrolysis;

V = dilution, or number of liters in which 1 gram equivalent is contained. $V=2$ in this case.

k_w = solubility or ionic product of water;

k_b = solubility or ionic product of AgOH.

$k_w=1.2\times10^{-14}$;

$k_b=2\times10^{-8}$.

When hydrolysis is slight,

$$\frac{\alpha^2}{V}=\frac{k_w}{k_b}=\frac{1.2\times10^{-14}}{2\times10^{-8}}=0.6\times10^{-6}$$

$$\alpha=\sqrt{1.2\times10^{-6}}=1.1\times10^{-3}$$

Therefore, theoretically about one-thousandth of the total amount of $AgNO_3$ in solution is hydrolyzed according to the following reaction:

$$AgNO_3+H_2O \rightleftarrows AgOH+HNO_3$$

The actual hydrolysis, of course, is much less than this; probably about 1.3×10^{-6}, as indicated by the intensity of color produced by methyl orange. The concentration was found to be too slight to affect the rate of hydrolysis of cane sugar by as much as 0.1 per cent in one day. Its effect upon the potential of the hydrogen electrode has not been determined. It is our present intention to apply this method at some future time.

to the ideal concentration of hydrogen ions in the electrolyte will be discussed in a later paper.

The usual methods of testing the neutrality of salts do not apply to silver nitrate solutions. Thus, toward litmus silver nitrate solutions react alkaline, even after the addition of 1 part in 100 000 of nitric acid, while the same sample will show an acid reaction toward methyl orange, even after the addition of an unlimited amount of alkali, so long as any undecomposed silver nitrate remains (i. e., so long as the Ag is not completely precipitated as AgOH). (For further details, see p. 247 of Part II of this series.) Toward phenolphthalein silver nitrate solutions show an acid reaction in the absence of carbon dioxide. So far as we are aware, all the data in the literature on the acidity of the electrolyte, except those by Leduc,[11] were obtained by litmus or other similar indicators applied directly in the usual way and can not therefore be relied upon for the reasons just given.

The following method of estimating the "uncombined" acid or base in silver nitrate is free from any uncertainties connected with the exact estimation of the absolute hydrogen ion concentration of solutions of partially hydrolized salts. The standards of neutrality used are the purest water obtainable, and solutions of the chlorides and nitrates of sodium or potassium in this pure water. These standards are as nearly absolute as can be realized experimentally, where a salt solution of some kind is necessary. The indicator chosen was iodeosine.[12] This is an exceedingly sensitive indicator (when used in ether-water solution) and may be readily used in titrating with thousandth normal solutions. The indicator is colorless in acid and pink in alkaline solution. The neutral point is unaffected, even by fairly concentrated solutions of pure sodium or potassium chloride (or nitrate); yet a single drop of a 0.001N solution of acid or alkali added to 10 cc of neutral solution is quite sufficient to cause a pronounced change in color. Its behavior toward acids and bases of different strengths is similar to that of methyl orange. In the present work it has been used only for titrating sodium hydroxide with either sulphuric or nitric acid. It is not necessary to expel the carbonic

[11] This Bulletin, 9, p. 159; 1912. [12] Förster and Mylius: Zs. anal. Ch., 31, p. 248; 1892.

acid before titration, since the end point is not affected by the amounts ordinarily present.

If the Ag be precipitated as AgCl by means of neutral recrystallized KCl or NaCl solution, and the AgCl filtered off through asbestos, the filtrate shows a neutral reaction toward all indicators if the original $AgNO_3$ contained no "uncombined" acid or alkali. Samples of silver nitrate purified by repeated recrystallization have been obtained which show a practically neutral reaction toward iodeosine when tested in this manner, *whereas if so little as one part in one million of nitric acid (or alkali) be added to the original solution*, it can be detected in the filtrate from the precipitated AgCl. In testing for amounts of acid less than several parts in one hundred thousand the AgCl must be filtered off by means of asbestos or finely divided platinum instead of filter paper, for the reason that pure distilled water extracts a small amount of oxycelluloses and cellulose hydrates from filter paper which show basic reaction toward iodeosine and methyl orange.

2. PREPARATION OF REAGENTS.

Iodeosine Solution.—About 500 cc of ordinary ether is shaken up with one-tenth its volume of dilute sodium hydroxide solution (5 per cent) in a separatory funnel, and the aqueous layer run off. The ether is then washed two or three times with distilled water in the same manner, using about one-tenth its volume of water each time. From 2 to 5 mg of iodeosine is dissolved in this washed ether. The solution is kept in a glass-stoppered bottle in contact with about one-tenth its volume of water. On long standing (two or three weeks) the iodeosine decomposes to a considerable extent. This is indicated by a diminution in its sensitiveness toward 0.001 N acid or base. A fresh solution should then be prepared.

Potassium Chloride Solution.—Prepare a 10 per cent solution from pure recrystallized potassium chloride and "conductivity" water. This solution should show an approximately neutral reaction toward iodeosine (the amount of base or acid, expressed in terms of HNO_3, should not exceed one part in a million).

Thousandth Normal Nitric Acid and Thousandth Normal Alkali.—Prepare by diluting 0.1 N or 0.01 N solutions that have been

standardized in the usual way. It is not necessary to exclude carbon dioxide. Fresh solutions should be prepared from time to time on account of the solubility of the glass containers.

3. DETAILS OF THE TEST FOR ACID OR BASE

10 cc of the silver nitrate solution to be tested is measured into a 100 cc beaker by means of a pipette or graduate, and just enough of the KCl solution added to completely precipitate the whole of the silver as silver chloride. This precipitate is removed by means of a filter of asbestos or finely divided platinum. If asbestos is used, *any appreciable excess of KCl solution must be avoided* since it reacts with the asbestos, forming acid salts which appear in the filtrate. (The potassium nitrate formed in the precipitation of the silver chloride has no such action upon the asbestos.) Not more than from 3 to 5 drops of KCl solution in excess of the amount required to exactly precipitate the whole of the silver as silver chloride should be used.

If the acidities are more than about 1 part in 100 000, the amount of acid left adhering to the precipitate and the filter mat can not be neglected. Either of two procedures may be followed—(1) the precipitate and filter mat may be washed two or three times with a small volume of neutral water, so as to recover all the acid and the titration then made with the total volume of the filtrate; (2) 10 cc of the filtrate may be taken (without washing the precipitate and filter mat) and a correction applied for the difference in volume between 10 cc and the total volume before filtration. These two methods have been found to agree in practice.

Before use, the filter and all glass vessels should be tested as to their effect upon the neutrality of "conductivity" water. This is done by determining the basicity (or acidity) of the water before and after contact with the glass vessels or filtration through the filter. Good conductivity water (conductivity less than 1.5×10^{-6}) from final distillation from alkaline permanganate is usually basic to the extent of about 0.6 parts in a million, as determined by titration with 0.001 N acid, using iodeosine indicator in the manner described below. The change in basicity caused by filtration or contact with glass vessels (for the time

usually occupied in a regular determination) should not exceed 0.3 parts in a million.

The titration is carried out in a 25 cc glass stoppered cylinder of resistant glass in the following manner: Two cc of distilled water and 4 to 10 cc of the ether solution of iodeosine are first placed in the cylinder. This aqueous-ether solution is neutralized by the addition of 0.001 N acid or alkali until 1 or 2 drops of the 0.001 N solution is sufficient to change the solution from colorless to a very distinct pink, or vice versa, after vigorous shaking. If this change is not sharp, it indicates that not enough iodeosine is present in the ether solution or that the iodeosine has partially decomposed, in which case a fresh solution should be prepared. Ten cc of the solution to be tested is now added to this *neutral* solution of the indicator and neutralized by the addition of 0.001 N acid or base. Or, if preferred, 40 or 50 cc of the ether solution may be neutralized in a stoppered cylinder and used as required. Each cc of the 0.001 N solutions contains 0.000063 g in terms of nitric acid. Hence, for a 10 cc sample, the number of parts per million in the solution tested is given by multiplying the number of cc of solution required for neutralization by the factor 6.3. The value thus obtained is corrected for the amount of acid or base present (if any) in the known volume of KCl solution used. This value for the KCl solution must be determined before and after each series of determinations, since it tends to become slowly more basic, due to its action on the glass container. If the asbestos or glass vessels are shown to be appreciably soluble by the test with conductivity water, already described, correction for the amount of base (or acid) so dissolved must also be applied by making a blank determination with conductivity water, using the same volume as used in a regular determination and allowing the same time of contact with the vessels and filter. The solubility of the vessels and asbestos filter is usually so very slight in the time required for a determination that it can be entirely neglected; if it is appreciable, more resistant glassware should be obtained. If asbestos is used for filtering, 5 cc of the KCl solution and 10 cc of *neutral* double-distilled water is added directly (without filtration) to the neutral aqueous-ether solution of the indicator in the titration cylinder;

the amount of 0.001 N solution required for neutralization does not usually exceed 0.1 cc (if more than this is required, the KCl is unfit for use and a more nearly neutral sample of recrystallized KCl should be prepared).

D. PERMANGANATE TEST FOR COLLOIDAL SILVER AND OTHER REDUCING IMPURITIES IN SILVER NITRATE

1. OBJECT OF THE TEST

In the early part of present investigation (July, 1909) the behavior of various electrolytes toward thousandth normal permanganate solution was investigated in the hope that it would afford some clue as to the cause of the marked differences in the results obtained with the various types of voltameters then in use. It was suspected that these discrepancies were in some way connected with the presence of impurities of a reducing nature formed either by the action of organic septa or possibly by secondary reactions at the anode as postulated by Richards, Collins, and Heimrod.

Further development of this test resulted in a method of detecting these highly objectionable reducing impurities that proved to be far more sensitive and of much wider application than had been expected from it at first.

The greatest value of the permanganate test is in detecting minute traces of colloidal metallic silver which may be formed in the process of fusing pure silver nitrate even when this is done with great care. We know of no other test which is so sensitive for this purpose. This test, together with the neutrality test described in the preceding section, has made it possible to specify a standard degree of purity of fused silver nitrate for use in the voltameter. As will appear later, this can not be safely done by fixing the conditions of fusion in respect to temperature, time of fusion, etc.

The test has also been of great use in estimating the degree of contamination of commercial samples of silver nitrate with organic material.

2. PREPARATION OF SOLUTIONS

Thousandth Normal Permanganate Solution.—Dissolve 0.0316 g of crystals of potassium permanganate in distilled water and

dilute to 1 liter. This solution may be standardized by comparison with standard sodium oxalate. The solution is best preserved in the dark, and should be kept free from contamination with dust or organic material.

Concentrated Nitric Acid.—The best grade of commercial c p acid is satisfactory. It should be tested for reducing impurities as follows: 1 cc of the concentrated acid is diluted to 10 cc with double-distilled water (in glass-stoppered cylinder) and 1 cc of 0.001 N permanganate solution added; the pink color should persist for 20 minutes or longer. The concentrated acid must be kept in the dark or in a brown bottle and preferably in a cool place.

3. METHOD OF MAKING THE TEST

The test with permanganate is made as follows: 10 cc of a 66.6 per cent solution of the $AgNO_3$ to be tested is placed in a glass-stoppered cylinder of 25 cc capacity and acidified by the addition of 1 cc of concentrated nitric acid (free from reducing substances). After thorough mixing of the acid and solution, 0.5 cc of the 0.001 N permanganate is added and the whole again shaken to mix the solutions. The time required for the pink color to fade is noted. After the solution is colorless a second half cubic centimeter of the permanganate solution is added as before. The addition of the permanganate is continued in portions of one-half cubic centimeter until the color persists undiminished in intensity for five minutes or longer.

4. TESTING FOR ORGANIC IMPURITIES

For the detection of the more resistant forms of organic reducing impurities (principally cellulose hydrates from filter paper) the acid silver nitrate crystals should be first fused. The more reactive reduction products thus formed (principally colloidal silver) readily reduce permanganate. The amount of these more active reduction products formed (even from very resistant organic material) is sufficient to render the test a very sensitive one for the detection of organic material in general.

The reliability of the "fusion-permanganate test" as a means of detecting the presence in silver nitrate of reducing impurities not otherwise capable of detection by any method yet employed

(except perhaps the "volume effect" in the voltameter) is illustrated by the following tests (Table 14) applied to solutions containing *known amounts of cane sugar and filter paper extract (oxycelluloses)*. It will be seen that except where the silver separated in "massive condition" the "permanganate numbers" are approximately proportional to the amounts of organic material added and that exceedingly small traces can be detected in this way. The salt used was recovered from used solutions by evaporation and recrystallization from 10 per cent HNO_3 solution. The crystals were centrifugally drained and were, of course, strongly acid. After fusion in the manner described 10 cc of a 66.6 per cent solution required only 1 cc of thousandth normal permanganate to produce a color which persisted for longer than one-half hour. In the table, by "permanganate number" is meant the number of cubic centimeters of thousandth normal permanganate reduced by 10 cc of a 66.6 per cent solution of the fused silver nitrate, the fusion and test being made in the manner described. The filter paper extract was prepared by digesting about 3 g of Schleicher & Schull No. 597 filter paper in 25 cc of distilled water at 30° C for 10 minutes and filtering through a sheet of the same paper. Measured volumes of a standard solution of the impurity was added to a definite volume (30 cc) of a 66.6 per cent solution of the silver nitrate and the mixed solution was evaporated to dryness in a 50 cc platinum dish on the steam bath and then fused in the same dish.

TABLE 14

Amount and kind of impurity added	Permanganate number after fusion	Remarks
1 cc of filter paper extract	3.5	
2 cc of filter paper extract	5.0	
5 cc of filter paper extract	12.5	
0.1 cc of 0.5 per cent solution of cane sugar	3.0	
0.5 cc of 0.5 per cent solution of cane sugar	8.0	
1 cc of 0.5 per cent solution of cane sugar	13.0	Considerable gray metallic silver separated
5 cc of 0.5 per cent solution of cane sugar	35.0	Most of the silver separated as the ordinary gray metallic variety (non-colloidal)

It is not claimed, of course, that the organic material is *completely* oxidized to carbon dioxide (or carbon monoxide) and water, but the partial oxidation is sufficient to render the method very sensitive indeed as a means of detecting the presence of traces of organic reducing material. Thus, less than 0.001 per cent of cane sugar can be readily detected in this way; this corresponds to 0.0001 per cent in a 10 per cent solution of the salt. This, of course, is much more sensitive than any method of direct combustion would probably prove under the conditions, besides possessing very great advantages in the matter of expediency and simplicity. We have not yet definitely shown that the test is of universal application to all classes of organic substances, although it is capable of revealing very small amounts of even such a difficultly oxidizable substance as paraffin, so that it seems highly probable that no appreciable amount of organic material of any kind could escape the test. Certainly any reducing material sufficiently active to produce any reducing action upon silver nitrate solution could not possibly escape detection by this test. This is illustrated by the case of cane sugar mentioned above, for this substance has practically no reducing action whatever on silver nitrate solutions (Part II, p. 252); yet if silver nitrate containing traces of it be fused, sufficient colloidal silver is formed to enable it to be readily detected by the permanganate test. This test, together with the iodeosine test for "neutrality," has been a very important factor in increasing the *reproducibility* of the voltameter, the results being independent of the *source* of the material. Likewise the two tests mentioned have enabled us to obtain concordant results with silver nitrate purified by two different methods, (1) by recrystallization from faintly acid solution, (2) by recrystallization from strongly acid solution followed by fusion.

5. TESTING FOR COLLOIDAL SILVER

The following test shows the reliability of the permanganate test as a method of accurately estimating the amount of colloidal silver present in silver nitrate.

A colloidal silver solution prepared by Bredig's method (using conductivity water of the highest purity) was titrated first against a standardized solution of ammonium sulphocyanate, and then an

equal volume of the same solution was titrated against thousandth normal permanganate in the usual manner, allowing five minutes for the pink color to discharge itself. The agreement between the values was well within the experimental error.

25 cc of Bredig's silver hydrosol required 0.4 cc of $\frac{N}{100}$ NH_4CNS solution.

25 cc of Bredig's silver hydrosol required 3.75 cc of $\frac{N}{1000}$ $KMnO_4$ solution.

The calculated equivalent of 0.4 cc of $\frac{N}{100}$ NH_4CNS is 4 cc of $\frac{N}{1000}$ $KMnO_4$. The agreement would probably be closer with thousandth normal NH_4CNS solution instead of hundredth normal.

By titrating concentrated solutions of silver nitrate (60 to 70 per cent) with thousandth normal permanganate less than 0.001 per cent of colloidal silver may be detected in this manner.

As prviously stated, the test is particularly applicable to the detection and estimation of colloidal silver formed by "overfusion" of silver nitrate. That the reducing substance formed in this way is colloidal silver and not subnitrate is indicated by the appearance of solutions of the fused salt when examined under the ultramicroscope; the presence of colloidal particles is readily revealed in this way. Colorimetric estimation of the nitrites present in such fused salt shows that these are not present in amounts sufficient to account for an appreciable proportion of the permanganate reduced.

The permanganate test is equally applicable to the detection of reduced colloidal silver in recrystallized silver nitrate.

In testing recrystallized salt it is always advisable to test a portion of it with permanganate both before and after fusion. The test before fusion will indicate whether the process of recrystallization has been properly carried out, and the test upon the fused salt will reveal the presence of any organic material which may by accident have found its way into the material. In our further investigations no silver nitrate has been used in the voltameter without first being tested in this way. In addition great care was of course exercised in protecting the material from dust and other sources of contamination with organic material.

E. DISTILLATION AND TESTING OF THE WATER

1. METHOD OF DISTILLATION

The water used in making the electrolyte for the voltameters has been twice distilled. It has always been free from suspended matter and carefully kept in large stoppered bottles of resistant glass that have been in use for some years and now produce very little effeet on the conductivity of the water. The method of preparing the water has been as follows: Water from the city mains, having a conductivity of about 3×10^{-5}, is passed directly through an automatic regulator into a large block tin still having a daily capacity of 75 liters. The water is boiled by steam at 40 pounds pressure, passing through a coil in the container of the still. Before reaching the condenser the vapor passes through a bed of quartz to remove any particles of matter that might be carried over mechanically. After condensation the water is collected in a large glass carboy. The conductivity of this is from 3 to 6×10^{-6}.

The second distillation takes place in another still of smaller capacity. The first distilled water is rendered alkaline and potassium permanganate added before being put into the second still. Heat is supplied by steam under pressure as before. The water vapor passes through traps to catch any matter carried over mechanically, and then is condensed in block tin. The water is collected in a large glass receiver with a guard tube of soda lime and H_2SO_4. A considerable fraction of the distilled water is discarded at the beginning and end, only the middle portion being saved. Tests for ammonia are always made with Nessler's reagent, and from time to time we have made conductivity tests also. The conductivities have ranged from 0.85×10^{-6} to 2×10^{-6}, but were usually about 1.3×10^{-6}.

2. REQUIREMENTS AS TO CONDUCTIVITY, ALKALINITY, ETC.

As we lay great stress on the necessity for purity of the electrolyte in the silver voltameter, it is axiomatic that only the best water should be used. This precaution becomes of especial importance, because the impurities which increase the conductivity of the water are usually alkalis. We have found that alkali in the electrolytes, although not present in sufficient amounts to

show a precipitate, will nevertheless increase the deposit of silver and in some cases alter slightly the appearance of the deposit. We have measured the conductivities of distilled water containing known amounts of impurities and conclude that for work of the highest precision the water should not have a greater conductivity than 2.5×10^{-6}.

It sometimes happens that when neutral $AgNO_3$ is used the resulting solution will show a slight trace of alkalinity when tested with iodeosine, which is due to the alkalinity of the water itself. In some instances we have rendered such electrolytes slightly acid by the addition of pure nitric acid, but more recent tests have shown that this is a doubtful procedure. This is due to the fact that alkaline water absorbs or combines with larger quantities of carbon dioxide from the atmosphere than neutral water and the mere addition of acid does not, of course, expel the gas (unless the solution is boiled). We have found that free carbon dioxide in the electrolyte in some manner greatly increases the weight of silver deposited in the voltameter; consequently any procedure which tends to increase the normal amount of carbon dioxide which is unavoidably retained by the electrolyte (when working in an atmosphere of ordinary air) must be carefully avoided. The water should therefore be as nearly neutral as possible as it comes from the still. In testing the neutrality of the water a neutral solution of iodeosine in the ether-water mixture is prepared as described on page 529 and 10 cc of the water to be tested added to this and the titration made with thousandth normal acid or alkali as in testing any other solution.

The question as to the manner in which the carbon dioxide increases the weight of the electro-deposited silver will be given attention in a subsequent article.

F. STANDARD METHODS FOR THE PREPARATION OF SILVER NITRATE FOR USE IN THE VOLTAMETER

1. SOURCE OF MATERIAL

The methods of purification described on the following pages are intended to be applied only to silver nitrate, which is already of a fair degree of purity. Preferably it should conform to tests such as are given in any of the good manuals on the purity of

reagents. Most of the c p or "analyzed" salt obtained from the best manufacturers is satisfactory material with which to start. Of course any one of the special methods to be described may be repeated as often as desired, or until there is no further change in the values obtained in the voltameter; but in case the material does not conform to the tests referred to above it will save much labor first to recrystallize the salt from strongly acid solution until it does meet these requirements except as to neutrality and then remove the acid by one of the special methods of purification to be described.

If the salt is prepared from metallic silver and nitric acid, the excess acid must be removed either by the method of recrystallization or by fusion, both of which processes are described in detail below.

2. PURIFICATION BY RECRYSTALLIZATION

The very sensitive iodeosine test for uncombined acid and base, described in section C, shows that salt obtained by recrystallization from *neutral* water is slightly basic. This is especially true if fairly dilute solutions are concentrated by evaporation (even under diminished pressure) in order to cause a separation of crystals.

The formation of faintly basic crystals has been observed when quartz vessels were used and when every precaution was taken to insure the purity and especially the neutrality of the water. The amount of base present in crystals so prepared as determined by the iodeosine test has never been found to exceed two parts per hundred thousand in the solid salt or two parts per million in 10 per cent solution. Notwithstanding the fact that this trace of base may be negligible for most work, even of an exact nature, it can not be disregarded in work with the silver voltameter, because it gives rise to the "volume effect" which has been observed with electrolytes known to be contaminated with filter paper, added base, etc. In recrystallizing there is also a tendency for the salt to become slightly reducing in character (unless traces of acid are present). This is brought about by heating the solution. The greater part of the trouble experienced in the earlier work with salt recrystallized from neutral solution was probably due to the basic reaction of the crystals rather than to reducing impurities.

If the recrystallization is carried out with faintly acid solutions and the crystals drained until they are either exactly neutral or faintly acid (a few parts per 100 000), the process may be repeated until the salt does not show the "volume effect" and does not reduce permanganate. (See p. 516.)

Regulating the acidity of the solution so that the drained crystals are not basic, on the one hand, nor too strongly acid, on the other, is often rather difficult. Moreover, the yield of crystals is ordinarily not much greater than half of the salt taken. For these reasons it was found more convenient and more economical to first crystallize from strongly acid solution (10 per cent or more) and then expel the acid by fusion in the manner described in section G. *This was done, however, only after it had been found that the fusion process when properly regulated yields salt which gives the same results in the voltameter as the recrystallized salt.*

A solution which is neutral toward iodeosine remains neutral after heating at the temperature and for the length of time usually required in recrystallizing, yet the crystals obtained when the same solution is allowed to cool will show the basic reaction referred to above. This indicates that while the heating process may produce silver hydroxide (or basic silver nitrate), the equivalent amount of acid still remains in solution, and therefore after precipitating and removing the silver as silver chloride, the filtrate is still neutral toward iodeosine. This behavior, in our opinion, is due to a very slight hydrolysis of silver nitrate (p. 526) which is favored by the higher temperature. It is probable that the silver hydroxide (or basic nitrate) formed by hydrolysis at the higher temperature becomes colloidal and separates with the crystals.

The important requirement in purifying silver nitrate entirely by recrystallization is to have the mother liquor of the *final* crystallization sufficiently acid to prevent the crystals from becoming basic, but not sufficient to cause them to become too strongly acid for use in the voltameter (i. e., the crystals must not contain more than a few thousandths of 1 per cent of acid). The maximum acidity of the mother liquor that is permissible in the final crystallization depends a great deal upon the efficiency of the means used for draining the crystals, but is about 1 per cent for the most efficient centrifugal draining. On the other hand, the

minimum concentration of acid that will prevent the formation of basic crystals is approximately 0.1 per cent of the water used as solvent, although this also depends to some extent upon the temperature to which the solution is heated and upon the time of heating. The temperature should be regulated between 100° and 110° C (the boiling point of concentrated solutions is above these limits), and the time required for disintegrating the crystals ought not to exceed two hours. Crystallization by evaporation even at ordinary temperatures in vacuo does not, however, in our experience, prevent the crystals from becoming faintly basic when separated from perfectly neutral solution.

Best results have been obtained by recrystallization from solutions made acid to the extent of 0.5 per cent of the water used and draining the crystals obtained by means of a porcelain centrifuge, having a rotating basket approximately 15 cm in diameter and using 1200 r. p. m.[13]

The salt used in preparing electrolyte E (Report to International Committee, p. 158) was prepared in this way and contained 0.003 per cent nitric acid and showed no volume effect or permanganate reduction either before or after fusion. Data concerning various electrolytes from recrystallized salt prepared in this manner will be given in Part IV of this series. It was found that salt recrystallized first from 10 per cent nitric acid solution (with centrifugal draining) and then from neutral twice-distilled water contained just about the right amount of acid for use in the voltameter (i. e., from 0.001 per cent to 0.003 per cent of the solid salt).

All but the final crystallization may, of course, be made from strongly acid solution. This is advisable, not only because of the greater yield obtained, but also because it seems to facilitate the removal of reducing impurities, so that fewer crystallizations are required to give a satisfactory product.[14]

The crystallization is carried out in porcelain, quartz, or platinum vessels. No differences have ever been observed in the

[13] If a centrifuge is not available, the draining may be accomplished by means of a porcelain funnel with perforated draining plate fitted to an ordinary filtering bottle, which has been thoroughly leached out. In fact, a preliminary draining by this means is a helpful adjunct to centrifugal draining, especially if the solution has been cooled to increase the yield of salt, since the main portion of mother liquor can be quickly removed by this means before it has had time to dissolve more salt in warming to room temperature.

[14] If the salt is strongly contaminated with filter paper or other organic reducing material, a preliminary fusion until it begins to darken and is slightly basic lessens the number of crystallizations necessary.

results obtained with salt crystallized in vessels made of these several materials. We prefer porcelain vessels, since they are obtainable in a larger assortment of convenient sizes and shapes; and because of their lower cost one need not be handicapped by having to work with a limited number.

In dissolving crystals of silver nitrate it is best to heat the solution over a steam bath. A free flame should not be used. In some cases we have heated the beaker containing the solution in a cylindrical-shaped vertical electric furnace of sufficient depth to permit of the heating of the solution uniformly for about one-half its depth. The temperature was kept at about 120° C. The upper portion of the beaker should be protected from radiated heat by means of a sheet of asbestos provided with a circular opening to admit the beaker.

The yield from a single crystallization is greatly increased by cooling the mother liquor with an ice bath or freezing mixture, provided the crystals are immediately drained before they have time to redissolve as the solution warms up to the temperature of the room.

In crystallizing from strongly acid solution the yield may be further increased by adding the acid after the crystals have been dissolved in neutral water and before the solution has cooled sufficiently to cause a separation of the crystals. Addition of the acid causes an immediate separation of the larger portion of the salt in the form of very fine crystals. In this form they are more readily freed from excess nitric acid by draining.

3. PURIFICATION BY RECRYSTALLIZATION FROM NITRIC ACID FOLLOWED BY FUSION

The salt should first be recrystallized from strong nitric acid solution in the manner described in the preceding section and the process repeated until 10 cc of a 66.6 per cent solution of the well-drained crystals reduces not more than 1 cc of thousandth normal permanganate solution.

The crystals are then fused under conditions which insure the retention of a few thousandths of 1 per cent of the acid. The conditions of fusion which have been found to give the best results are described on page 549.

Ordinarily the product thus obtained will not have a permanganate number greater than two and will not show the volume effect or any other evidence of contamination with objectionable impurities. If the product reduces more than this amount of permanganate or shows other evidence of the presence of impurities, the salt must again be recrystallized from strongly acid solution and fused again in the same manner. This treatment (alternate crystallization and fusion) must be repeated until the final fused product conforms to the following requirements:

(*a*) It must contain not more than two parts nor less than 0.5 part of nitric acid in one hundred thousand parts of solid salt (or in one million parts of a 10 per cent solution). It is not difficult to realize this requirement if the fusion is carried out as described on page 549, since the process of fusion expels all but about this amount of acid.

(*b*) A 10 cc sample of a 66.6 per cent solution must not decolorize more than 2 cc of 0.001 N permanganate solution, the permanganate being added one-half cubic centimeter at a time and five minutes allowed to elapse after the addition of each portion.

Before dissolving the fused salt (in preparing the electrolyte) the surface is washed by placing the solid cake in a funnel and quickly pouring sufficient water over it to remove a thin outer layer of the salt. This addition to the process of preparing the electrolyte was suggested and first used by Mr. F. E. Smith of the National Physical Laboratory. The object was to remove any possible traces of dust or other impurities which may have collected on the surface. We have found that in cases of *badly contaminated silver nitrate* this washing process also sometimes removes a considerable portion of the reducing substances (probably finely divided metallic silver or coagulated colloidal silver) which is found to accumulate on the surface. This is indicated by the fact that in some such instances we have observed that these surface washings reduce appreciable amounts of thousandth normal permanganate, whereas the washings from the interior of the fused cake may reduce much less permanganate than that from the surface. For this reason washing the surface may sometimes shorten the purifying process. The chief value of the process of fusing the salt, however, lies in the aid it gives in quickly removing the excess acid and more important still, the very sensitive and

convenient means it affords in connection with the permanganate test, of *detecting the presence of colloidal silver and also any reducing impurities* which are so objectionable in voltameter work.

4. PURIFICATION OF USED SOLUTIONS

In preparing pure silver nitrate from old used solutions, especially those strongly contaminated with filter paper or which had been stored in glass containers for several months, we have in some cases evaporated the solutions completely to dryness in porcelain vessels, and subsequently fused until the melt darkened slightly. This treatment decomposes any organic reducing material present and renders most of the silica, iron, etc. (from the glassware) insoluble.

The solid was then dissolved in hot distilled water without the addition of acid and filtered through asbestos to free it from the greater portion of silica and insoluble oxides. This material when crystallized from 10 per cent nitric acid solution, centrifugally drained in a porcelain centrifuge and fused, usually gave a satisfactory product; if not, it was recrystallized from 10 per cent nitric acid, drained, and fused again. This second treatment has always yielded a satisfactory product.

If the solution is not too strongly contaminated, the mother liquor may be evaporated again and a second crop of crystals obtained, or, as suggested by Mr. F. E. Smith, it may be used as a solvent for other salt to be purified in the same manner.

5. PROTECTION FROM DUST

During all the processes of preparing the salt, it was protected from any appreciable contamination with dust by means of cover glasses or inverted crystallizing dishes, which were kept over the salt or solution except when the transferring of the salt from one container to another prevented, and even in these cases a large cover glass was held above the vessels and between the operator and the material. We have never observed, however, that short exposure to the usual conditions of the atmosphere (provided it is free from fumes) has in any way affected the properties of the salt as shown by the chemical tests described (neutrality and reducing properties) or by the values obtained with the voltameter, and therefore believe this is only a minor source of contamination as compared to those discussed at the beginning of this chapter.

G. FUSION OF SILVER NITRATE

1. EFFECT OF PROLONGED FUSION AT TEMPERATURES NEAR THE MELTING POINT

The first fused silver nitrate prepared in the present work was fused under conditions which were, as nearly as practicable, the same as described by Richards and Forbes [15] in their work on the atomic weight of nitrogen. The salt was prepared by dissolving very pure metallic silver in redistilled nitric acid. Several samples of silver from different sources were used and led to the same results.

The product obtained did not, however, prove satisfactory for voltameter work, since it reduced appreciable amounts of thousandth normal permanganate (14 g reducing from 3 to 4 cc), and in 50 per cent solution even *gave a striated deposit when electrolyzed.* It was therefore concluded that the acid could not be completely expelled by fusion without slightly decomposing the salt into metallic silver, which, of course, is to be avoided above all other impurities in voltameter work.

At the time these fusions were made the iodeosine test for neutrality had not been fully developed, and we had not yet discovered that fusion for a much shorter time suffices to remove the free acid (although not all the moisture and air). The fusion method was therefore abandoned for the time and recourse had to the method of recrystallization.

While it appeared possible that these unsatisfactory results might have been due to failure on our part to exactly duplicate the conditions described by Richards and Forbes, it was apparent that if this were so the *limits* within which the conditions could be safely varied must be very narrow; too narrow, indeed, to render the process free from grave danger of introducing contaminations into the electrolyte.

It seems that no such narrow limitations apply to the method of fusing, if the sole object is to determine the mass of the salt for purposes of atomic weight work. This was admirably demonstrated by Richards and Forbes, who showed that the salt could be kept in a fused condition at 210° C for several hours longer than the usual time which they employed without suffering loss in weight, or it could be redissolved, evaporated, and fused again

[15] J. Am. Ch. Soc., 29, p. 808.

without undergoing any change in weight which was sufficient to affect their results. In such cases [16] the salt sometimes became slightly darkened, yet without suffering significant loss in weight. On the other hand, it has been observed many times in the present investigation that if fused salt is discolored, even only slightly, it will give a *pronounced* volume effect and will yield a striated deposit with the accompanying high value for the electrochemical equivalent of silver. This is due to the *magnified* effect produced by mere traces of reducing impurities (and colloidal silver) in the voltameter.

It does not seem necessary to further describe the conditions of fusion in this earlier work in which the attempt was made to duplicate the conditions of Richards and Forbes, except to state that great care was exercised in excluding all organic material and special precautions were taken to have the temperature of the oven uniform in order that the actual temperature at which the fusion was carried out could be accurately determined. The only conditions differing from those described by Richards and Forbes that were knowingly altered consisted in the use of a quartz evaporating dish instead of the quartz flask used in their work. This was done because a quartz flask was not available at the time. When the evaporating dish was used, the salt was protected from dust by means of an inverted funnel clamped in position just above the dish; the stream of dry and dust-free air entered through a delivery tube which passed through the funnel stem. The circumstance that in the present work it was not necessary to carefully guard against loss of silver by spattering simplified the procedure enormously. The unsatisfactory behavior in the voltameter of salt fused *under these conditions* has already been described.

2. FACTORS THAT INFLUENCE THE DECOMPOSITION OF SILVER NITRATE WHEN FUSED

Whether silver nitrate is decomposed by heat when fused seems to depend less upon the temperature than upon the amount of acid retained by the melted salt. As soon as the last trace of acid is expelled the salt begins immediately to decompose into silver oxide and colloidal metallic silver. This is indicated by the basic reac-

[16] J. Amer. Chem. Soc., **29**, pp. 814-815. We have obtained the same results.

tion of the salt toward iodeosine (after precipitating the silver as chloride with neutral potassium chloride) and its reducing action upon thousandth normal permanganate. If a trace of acid is retained by the salt, or if, as happens only rarely, it shows an exactly neutral reaction, the product does not reduce appreciable amounts of permanganate and shows no "volume effect" (p. 514).

In all cases, salt which after fusion was found to reduce appreciable amounts of thousandth normal permanganate also showed a faint basic reaction (except when it contained organic material, in which case it always showed unmistakable evidence of reduction to metallic silver, even though the fusion were carried out in such a manner that the fused salt retained quite appreciable amounts of uncombined acid). Fused salt which showed no evidence of such reduction was usually faintly acid (containing from 0.0005 per cent to 0.005 per cent), but occasionally was exactly neutral, or, in a few instances, faintly basic.[17] In the latter case evidently a portion of the salt had been decomposed into silver oxide which had not yet undergone further decomposition into metallic silver and oxygen.

After the last traces of nitric acid have been expelled the rate of decomposition depends chiefly upon the temperature. If the temperature is kept within 2° or 3° of the melting point, which is approximately 208° C., the rate of decomposition is so slight that, as shown by Richards and Forbes, the salt may be kept in a fused condition for an hour or longer without suffering appreciable loss in weight. However, our own results show that the amount of metallic (colloidal) silver formed under these conditions may amount to as much as 0.002 per cent. At 10° to 20° above the melting point the rate of decomposition is probably more than twice as rapid as at its melting point (see p. 548), although, according to some preliminary tests, the loss in weight, even under these conditions, does not seem to be appreciable. But the amount of decomposition as determined by the permanganate and iodeosine tests has been determined under these and several other different sets of conditions (see p. 548), and is quite appreciable under the conditions last mentioned. It is our belief, therefore, that quite appreciable decomposition can take

[17] See Table 15, p. 548.

place without a corresponding loss in weight, due perhaps to the retention by the salt of some of the gaseous products of decomposition.

Salt which has been fused at 230° C. and removed as soon as melted, although neutral, still contains quite appreciable amounts of moisture, dissolved air, etc., as is indicated by the fact that further fusion at the lowest possible temperature causes a relatively large decrease in weight; sometimes this loss is as much as 0.02 per cent, and yet the decomposition as shown by the permanganate test is *nil* in comparison. This shows the necessity of longer fusion, if the mass of the pure salt is to be determined accurately for atomic weight determinations, although it is certainly objectionable if the salt is to be used in voltameter work of the highest precision. After it was found that practically every trace of acid is expelled as soon as the salt is completely fused and that no other sources of error are involved, the method of expelling the excess acid by fusion (instead of recrystallization) was employed almost exclusively because of its greater convenience and economy. Also it is much easier by this method to prevent the formation of basic salt (or oxide) than when the acid is removed by recrystallization. If the crystals are strongly acid, the time required to completely melt the salt apparently has very little effect upon the amount of acid retained; this is no doubt due partly to the fact that the temperature does not rise appreciably above the melting point of the salt until all of the solid has melted; but the principal reason is doubtless due to the gradual liberation of nitric acid included in the crystals as they slowly melt.

The following instances are given in tabular form and will serve to illustrate the effect of the various conditions of fusing, both upon the amount of acid retained and also upon the permanganate reduction shown by the various samples. These are but a few instances chosen from a very large number of cases in which not all of the conditions were made a matter of record, but in which the same effects of the various conditions have been repeatedly observed with samples of salt which the various tests (including the volume effect in the voltameter) showed to be free from reducing impurities. So far as our own experience goes we have

not yet succeeded in keeping 100 g of salt or less in a state of fusion for longer than 15 minutes at a temperature of 230° (or more) without its becoming slightly basic. At the same time silver nitrate so fused has always shown permanganate reduction, whereas the same sample fused in such manner as to retain a slight amount of acid will show no such reduction. The limits of temperature and time of fusion within which the fusion may be made with reasonable safety are fairly wide. This is illustrated in part at least by the table given below. But the only safe procedure is to test *in every case* the fused salt, in order to be certain that it is slightly acid or at least that it is not basic, and that it does not reduce appreciable amounts of thousandth normal permanganate.

TABLE 15

Acidity Tests on Fused Silver Nitrate

[The acidity of the salt before fusion was about 0.1 per cent. Acidities after fusion are expressed in parts per million.]

Experiment No.—	Mass of salt fused	Temperature of oven	Time left in oven after completely fused	Acidity after fusion		Permanganate number after fusion	Remarks
				Acid	Basic		
	g	°C	min				
1	16	345	0.5	.....	1.5	1.0	Fused in 50 cc platinum dish
2	14	520	1	.....	2.0	6.5	Do.
3	14	345	2	.....	1.0	2.5	Do.
4	28	295	3.5	.....	1.0	2.0	Fused in 20 cc platinum crucible
5	30	318	1	0.3	.....	1.0	Fused in 50 cc quartz dish
6	30	230	30	.....	2.0	5.0	Do.
7[18]	15	230	15	.....	1.6	3.0	Do.
8	15	230	15	0.6	.....	1.0	Conditions same as in (7), except that fusion was made in 10 cc quartz test tube
9	15	230	30	0.5	.....	1.0	Fused in quartz flask of 50 cc capacity having neck 13 mm in diameter
10	15	230	30	.....	2.5	3.0	Fused in same flask as in (9), but with current of purified air flowing over surface of salt
11	15	250	60	.....	3.0	6.0	Fused in quartz dish (50 cc)
12	15	345	2	.....	1.6	4.0	Do.
13	100	350	0.5	.....	4.0	2.0	Fused in 175 cc platinum dish
14	100	350	0.5	.....	2.0	2.0	Do.

[18] Dried at 150° C for 15 minutes.

3. STANDARD CONDITIONS FOR FUSING SILVER NITRATE FOR USE IN THE VOLTAMETER

The most important condition to be observed in fusing silver nitrate for use in the voltameter is the maintenance of slightly acid condition throughout the process. The retention of acid in the melted salt whereby slight decomposition is avoided is accomplished by shortening as much as possible the time the salt remains in the fused condition and by reducing the rate of evaporation of acid from the surface of the fused salt.

The first of these objects has been accomplished in the main by removing the salt from the oven as soon as completely fused. Also it has been found practicable to fuse the salt at considerably higher temperatures than the melting point, thus shortening the time of fusion. The temperatures ordinarily employed have been between 250° and 300° C. There is no danger due to superheating at these temperatures when the salt is removed as soon as melted. The evaporation of acid is diminished by decreasing the surface relative to the mass of salt as much as practicable (i. e., deep vessels are used) and by dispensing with the current of air used by Richards and Forbes.[19]

Our best results have been obtained by fusing from 150 to 200 g of the strongly acid crystals in a platinum crucible of about 80 cc capacity (4 cm maximum diameter by 4.5 cm high), keeping the temperature of the oven between 250° and 300° C and removing the salt as soon as melted.

During the fusion, as well as all other processes in the preparation of the salt, it should be protected from dust, etc., by means of a cover glass. That organic material is efficiently excluded in this way is shown by the fact that if mere traces are added to the salt before fusion their presence is readily revealed by the reducing properties of the fused salt toward thousandth normal permanganate solution.[20]

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[19] Since only a relatively small volume of air comes in contact with the salt under these conditions (especially since the vessel is covered with a watch glass during the fusion), the chance of contamination with dust is no greater than that arising from the necessary exposure of the water and solutions to the air in preparing the electrolyte and during electrolysis. The principal object of the air current in the work of Richards and Forbes seems to have been to aid in the complete expulsion of water and of nitric acid. Since the acid is expelled without this precaution and since water is not objectionable in the present instance, there is no necessity of employing a current of air in the present case.

[20] It should be stated at this point that the first samples of *fused* salt which conformed to the permanganate and iodeosine tests were prepared by Mr. F. E. Smith, of the National Physical Laboratory, in

The fusion may be made in platinum or transparent fused quartz vessels. Platinum vessels are very convenient for this purpose and are not attacked by the fused silver nitrate, provided the above conditions of temperature of fusion and acidity of the salt are observed. Otherwise the silver nitrate may be partially decomposed (reduced), and the platinum becomes stained with silver. If by accident this happens the stains can be removed with fused sodium bisulphate or by fusing a second portion of silver nitrate in the same dish, taking care to observe the proper precautions in fusing. The attack of fused *alkaline* nitrates upon platinum is usually attributed to the active oxygen given off by the nitrate, but the $KMnO_4$ test shows that under the conditions which we have described this does not occur. Salt fused in either platinum or quartz vessels leads to the same result.

1910. Deposits made from repeatedly crystallized, faintly acid crystals agreed well with the deposits from this fused salt, and, as stated before, we consider this agreement very important evidence of the high degree of purity of the fused salt. At this time the conditions which bring about a decomposition of the salt had not been fully worked out, and the conditions under which the fusion could be made without danger of decomposition had not been definitely specified. Also the above tests for reducing impurities and for neutrality had not previously been applied to any fused salt except to the preparations made in the very early part of our own work, to which reference has already been made, and in these cases the results seemed to show that the process of fusion was a rather hazardous procedure.

Smith prepared the fused salt referred to by fusing large quantities (between 500 and 1000 g) of the strongly acid crystals in a covered electric furnace until about half of the salt was melted and then turned off the heating current; the temperature of the oven was not taken.

Application of the permanganate and iodeosine tests to salt fused under varying conditions later made it possible to define the conditions which give best results, and when these are observed the salt practically always conforms to the criteria mentioned. Occasionally a fused sample has been obtained which did not prove satisfactory and yet which we supposed had been prepared under proper conditions. This emphasizes the importance of *always* applying the chemical tests before using the salt in the voltameter, and indicates further that some of the conditions, probably the rate of evaporation of the excess nitric acid, are somewhat difficult to control. In this connection it might be mentioned that some of the samples of fused salt referred to above which were prepared by Mr. F. E. Smith were found to be faintly basic (before use in the voltameter), and one in particular, which gave a higher value in the voltameter than usual, was 2 in 10^6 basic. Our later experience makes it seem very probable indeed that this basic reaction was due to a very slight decomposition of the salt during the fusion (as we suggested at the time) rather than to the action of the solution upon the glass, as suggested by Smith. The change in neutrality of dilute silver nitrate solution, due to glass cleaned with ordinary care, is very seldom greater than 1 part per million after standing for a month or longer. Constant agitation of course greatly increases the effect, and this, together with the fact that very soft glass was used, probably accounts for the instance cited by Smith in the International Report where an electrolyte originally 1.8 acid became about 0.3 basic after constant agitation in a flask. Ordinarily with resistant thoroughly cleansed Jena glass, such as was used to store the electrolyte referred to above, the effect of the glass has been found to amount to less than a part per million, even on standing for several weeks. On the other hand, the formation of base by overfusion has been noted even after the important factors that produce decomposition had been determined and when these were specially guarded against. Moreover, in some such cases the decomposition seemed not to have progressed far enough to produce an objectionable amount of reducing impurities (colloidal silver), as indicated by the permanganate test, but apparently had stopped at the formation of a slight amount of silver oxide, which, however, would increase the weight of the deposit.

III. SUMMARY

1. Using the small porous cup voltameter the value 1.01827$_5$ volts has been found for the Weston Normal Cell at 20° C.

2. The difference between the values obtained with the large porous cup voltameter and the smaller sizes is due to impurities present in the electrolyte, which may be partially removed by electrolysis. This phenomenon has been called the "volume effect."

3. The temperature coefficient of the voltameter appears to be zero if the electrolyte is pure.

4. Deposits on gold and platinum cathodes are in agreement.

5. For testing the purity of silver nitrate special methods have been devised. Estimations of the acidity may be made to 1 part in 1 000 000, using iodiosine as an indicator in the manner described. For testing the solutions for reducing agents and colloidal silver $\frac{N}{1000}$ potassium permanganate has been successfully used.

6. Methods of preparing silver nitrate of a satisfactory purity have been found. These differ considerably from previous methods owing to the conditions demanded by the voltameter work.

7. The fusion of silver nitrate has been discussed at length with particular reference to the decomposition of the salt after all of the acid has been expelled.

WASHINGTON, January 1, 1913.